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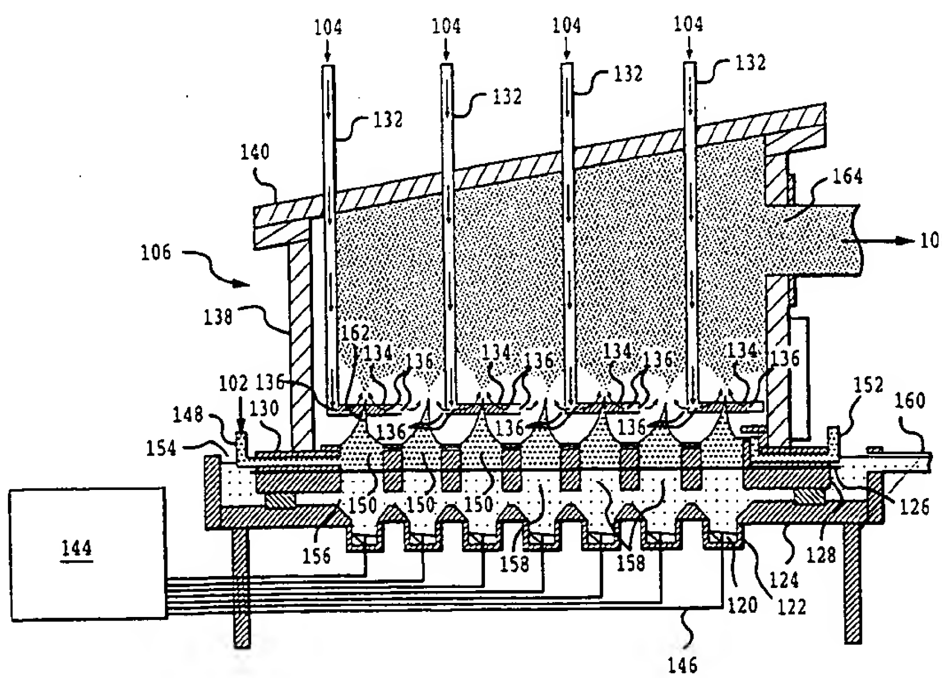

(57) Abstract

The invention relates to phosphor powders and a method for making phosphor powders. The powders are oxygen-containing, such as metal oxides, borates or titanates and have a small particle size, narrow particle size distribution and are substantially spherical. The method of the invention advantageously permits the continuous production of such powders. The invention also relates to improved devices, such as display devices, incorporating those shown by the figure, incorporating the phosphor powders.

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OXYGEN-CONTAINING PHOSPHOR POWDERS, METHODS FOR MAKING PHOSPHOR POWDERS AND DEVICES INCORPORATING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to oxygen-containing phosphor powders, methods for producing such powders and devices incorporating same. In particular, the present invention is directed to oxygen-containing phosphor powders having small average particle size, a narrow particle size distribution, high crystallinity and spherical morphology. The present invention also relates to a method for continuously producing such oxygen-containing powders and to devices that incorporate such powders.

2. Description of Related Art

Phosphors are compounds that are capable of emitting useful quantities of radiation in the visible and/or ultraviolet spectrums upon excitation of the material by an external energy source. Due to this property, phosphor compounds have long been utilized in cathode ray tube (CRT) screens for televisions and similar devices. Typically, inorganic phosphor compounds include a host material doped with a small amount of an activator ion.

More recently, phosphor powders have been utilized in many advanced display devices that provide illuminated text, graphics or video output, including flat panel display devices such as liquid crystal displays, plasma displays, thick film and thin film electroluminescent displays and field emission displays.

Liquid crystal displays (LCD's) use a low power electric field to modify a light path and are commonly used in wristwatches, pocket televisions, gas pumps, pagers and the like. Plasma displays utilize a gas trapped between transparent layers that emits ultraviolet light when excited by an electric field. The ultraviolet light stimulates phosphors on the screen to emit visible light. Plasma displays are particularly useful for larger displays, such as greater than about 20 diagonal inches. Thin film and thick film electroluminescent displays (TFEL's) utilize a film of phosphorescent material trapped between glass plates and electrodes to emit light in an electric field. Such displays are typically used in commercial transportation vehicles, factory floors and emergency

rooms. Field emission displays (FED's) are similar in principle to CRT's, wherein electrons emitted from a tip excite phosphors, which then emit light of different color.

Phosphor powders are also utilized in electroluminescent lamps (EL's), which include phosphor powder deposited on a polymer substrate which emits light when an electric field is applied.

There are a number of requirements for phosphor powders, which can vary dependent upon the specific application of the powder. Generally, phosphor powders should have one or more of the following properties: high purity; high crystallinity; small particle size; narrow particle size distribution; spherical morphology; controlled surface chemistry; homogenous distribution of the activator ion; good dispersibility; and low porosity. The proper combination of the foregoing properties will result in a phosphor powder with high luminescent intensity and long lifetime that can be used in many applications. It is also advantageous for many applications to provide phosphor powders that are surface passivated or coated, such as with a thin, uniform dielectric or semiconducting coating.

Numerous methods have been proposed for producing oxygen-containing phosphor particles. One such method is referred to as the solid-state method. In this process, the phosphor precursor materials are mixed in the solid state and are heated so that the precursors react and form a powder of the phosphor material. For example, U.S. Patent No. 4,925,703 by Kasenga et al. discloses a method for the production of a manganese activated zinc silicate phosphor. The method includes a step of dried blending a mixture of starting components such as zinc oxide, silicic acid and manganese carbonate and firing the blended mixture at about 1250°C. The resulting phosphor is broken up or crushed into smaller particles. Solid-state routes, and many other production methods, utilize such a grinding step to reduce the particle size of the powders. The mechanical grinding damages the surface of the phosphor, forming dead layers which inhibit the brightness of the phosphor powders.

Phosphor powders have also been made by liquid precipitation. In these methods, a solution which includes phosphor particle precursors is chemically treated to precipitate phosphor particles or phosphor particle precursors. These particles are typically calcined at an elevated temperature to produce the phosphor compound. The particles must often be further crushed, as is the case with solid-state methods. In yet another method,

phosphor particle precursors or phosphor particles are dispersed in a solution which is then spray dried to evaporate the liquid. The phosphor particles are thereafter sintered in the solid state at an elevated temperature to crystallize the powder and form a phosphor. For example, U.S. Patent No. 4,948,527 by Ritsko et al. discloses a process for producing Y_2O_3:Eu phosphors by dispersing yttrium oxide in a europium citrate solution to form a slurry which is then spray dried. Spray dried powder was then converted to an oxide by firing at about 1000°C for two hours and then at 1600°C for about four hours. The fired powder was then lightly crushed and cleaned to recover useful phosphor particles.

Despite the foregoing, there remains a need for oxygen-containing phosphor powders with high luminescent intensity that include particles having a substantially spherical morphology, narrow particle size distribution, a high degree of crystallinity and good homogeneity. The powder should have good dispersibility and the ability to be fabricated into thin layers having uniform thickness, resulting in a device with high brightness.

SUMMARY OF THE INVENTION

The present invention provides improved oxygen-containing phosphor powder batches having a small particle size, narrow particle size distribution, spherical morphology and good crystallinity. The present invention also provides methods for forming such oxygen-containing phosphor powder batches and devices incorporating such powder batches.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a process block diagram showing one embodiment of the process of the present invention.

Fig. 2 is a side view in cross section of one embodiment of aerosol generator of the present invention.

Fig. 3 is a top view of a transducer mounting plate showing a 49 transducer array for use in an aerosol generator of the present invention.

Fig. 4 is a top view of a transducer mounting plate for a 400 transducer array for use in an ultrasonic generator of the present invention.

Fig. 5 is a side view of the transducer mounting plate shown in Fig. 4.

Fig. 6 is a partial side view showing the profile of a single transducer mounting receptacle of the transducer mounting plate shown in Fig. 4.

Fig. 7 is a partial side view in cross-section showing an alternative embodiment for mounting an ultrasonic transducer.

Fig. 8 is a top view of a bottom retaining plate for retaining a separator for use in an aerosol generator of the present invention.

Fig. 9 is a top view of a liquid feed box having a bottom retaining plate to assist in retaining a separator for use in an aerosol generator of the present invention.

Fig. 10 is a side view of the liquid feed box shown in Fig. 5.

Fig. 11 is a side view of a gas tube for delivering gas within an aerosol generator of the present invention.

Fig. 12 shows a partial top view of gas tubes positioned in a liquid feed box for distributing gas relative to ultrasonic transducer positions for use in an aerosol generator of the present invention.

Fig. 13 shows one embodiment for a gas distribution configuration for the aerosol generator of the present invention.

Fig. 14 shows another embodiment for a gas distribution configuration for the aerosol generator of the present invention.

Fig. 15 is a top view of one embodiment of a gas distribution plate/gas tube assembly of the aerosol generator of the present invention.

Fig. 16 is a side view of one embodiment of the gas distribution plate/gas tube assembly shown in Fig. 15.

Fig. 17 shows one embodiment for orienting a transducer in the aerosol generator of the present invention.

Fig. 18 is a top view of a gas manifold for distributing gas within an aerosol generator of the present invention.

Fig. 19 is a side view of the gas manifold shown in Fig. 18.

Fig. 20 is a top view of a generator lid of a hood design for use in an aerosol generator of the present invention.

Fig. 21 is a side view of the generator lid shown in Fig. 20.

Fig. 22 is a process block diagram of one embodiment in the present invention including an aerosol concentrator.

Fig. 23 is a top view in cross section of a virtual impactor that may be used for concentrating an aerosol according to the present invention.

Fig. 24 is a front view of an upstream plate assembly of the virtual impactor shown in Fig. 23.

Fig. 25 is a top view of the upstream plate assembly shown in Fig. 24.

Fig. 26 is a side view of the upstream plate assembly shown in Fig. 24.

Fig. 27 is a front view of a downstream plate assembly of the virtual impactor shown in Fig. 23.

Fig. 28 is a top view of the downstream plate assembly shown in Fig. 27.

Fig. 29 is a side view of the downstream plate assembly shown in Fig. 27.

Fig. 30 is a process block diagram of one embodiment of the process of the present invention including a droplet classifier.

Fig. 31 is a top view in cross section of an impactor of the present invention for use in classifying an aerosol.

Fig. 32 is a front view of a flow control plate of the impactor shown in Fig. 31.

Fig. 33 is a front view of a mounting plate of the impactor shown in Fig. 31.

Fig. 34 is a front view of an impactor plate assembly of the impactor shown in Fig. 31.

Fig. 35 is a side view of the impactor plate assembly shown in Fig. 34.

Fig. 36 shows a side view in cross section of a virtual impactor in combination with an impactor of the present invention for concentrating and classifying droplets in an aerosol.

Fig. 37 is a process block diagram of one embodiment of the present invention including a particle cooler.

Fig. 38 is a top view of a gas quench cooler of the present invention.

Fig. 39 is an end view of the gas quench cooler shown in Fig. 38.

Fig. 40 is a side view of a perforated conduit of the quench cooler shown in Fig. 38.

Fig. 41 is a process block diagram of one embodiment of the present invention including a particle coater.

Fig. 42 is a block diagram of one embodiment of the present invention including a particle modifier.

Fig. 43 shows cross sections of various particle morphologies of some composite particles manufacturable according to the present invention.

Fig. 44 shows a side view of one embodiment of apparatus of the present invention including an aerosol generator, an aerosol concentrator, a droplet classifier, a furnace, a particle cooler, and a particle collector.

Fig. 45 illustrates a photomicrograph of an oxygen-containing phosphor powder according to an embodiment of the present invention.

DESCRIPTION OF THE INVENTION

The present invention is generally directed to oxygen-containing phosphor powders and methods for producing the powders, as well as devices which incorporate the powders. As used herein, oxygen-containing phosphor powders, particles and compounds are those which incorporate a host material that is an oxygen-containing compound, including metal oxides, silicates, borates or aluminates. Specific examples of such oxygen-containing phosphor compounds are detailed hereinbelow.

In one aspect, the present invention provides a method for preparing a particulate product. A feed of liquid-containing, flowable medium, including at least one precursor for the desired particulate product, is converted to aerosol form, with droplets of the medium being dispersed in and suspended by a carrier gas. Liquid from the droplets in the aerosol is then removed to permit formation in a dispersed state of the desired particles. Typically, the feed precursor is pyrolyzed in a furnace to make the particles. In one embodiment, the particles are subjected, while still in a dispersed state, to compositional or structural modification, if desired. Compositional modification may include, for example, coating the particles. Structural modification may include, for example, crystallization, recrystallization or morphological alteration of the particles. The term powder is often used herein to refer to the particulate product of the present invention. The use of the term powder does not indicate, however, that the particulate product must be dry or in any particular environment. Although the particulate product is typically manufactured in a dry state, the particulate product may, after manufacture, be placed in a wet environment, such as in a paste or slurry.

The process of the present invention is particularly well suited for the production of particulate products of finely divided particles having a small weight average size. In addition to making particles within a desired range of weight average particle size, with the present invention the particles may be produced with a desirably narrow size distribution, thereby providing size uniformity that is desired for many applications.

In addition to control over particle size and size distribution, the method of the present invention provides significant flexibility for producing particles of varying composition, crystallinity and morphology. For example, the present invention may be used to produce homogeneous particles involving only a single phase or multi-phase particles including multiple phases. In the case of multi-phase particles, the phases may be present in a variety of morphologies. For example, one phase may be uniformly dispersed throughout a matrix of another phase. Alternatively, one phase may form an interior core while another phase forms a coating that surrounds the core. Other morphologies are also possible, as discussed more fully below.

Referring now to Fig. 1, one embodiment of the process of the present invention is described. A liquid feed 102, including at least one precursor for the desired particles, and a carrier gas 104 are fed to an aerosol generator 106 where an aerosol 108 is produced. The aerosol 108 is then fed to a furnace 110 where liquid in the aerosol 108 is removed to produce particles 112 that are dispersed in and suspended by gas exiting the furnace 110. The particles 112 are then collected in a particle collector 114 to produce a particulate product 116.

As used herein, the liquid feed 102 is a feed that includes one or more flowable liquids as the major constituent(s), such that the feed is a flowable medium. The liquid feed 102 need not comprise only liquid constituents. The liquid feed 102 may comprise only constituents in one or more liquid phase, or it may also include particulate material suspended in a liquid phase. The liquid feed 102 must, however, be capable of being atomized to form droplets of sufficiently small size for preparation of the aerosol 108. Therefore, if the liquid feed 102 includes suspended particles, those particles should be relatively small in relation to the size of droplets in the aerosol 108. Such suspended particles should typically be smaller than about 1 μm in size, preferably smaller than about 0.5 μm in size, and more preferably smaller than about 0.3 μm in size and most preferably smaller than about 0.1 μm in size. Most preferably, the suspended particles

should be able to form a colloid. The suspended particles could be finely divided particles, or could be agglomerate masses comprised of agglomerated smaller primary particles. For example, 0.5 μm particles could be agglomerates of nanometer-sized primary particles. When the liquid feed 102 includes suspended particles, the particles typically comprise no greater than about 25 to 50 weight percent of the liquid feed.

As noted, the liquid feed 102 includes at least one precursor for preparation of the particles 112. The precursor may be a substance in either a liquid or solid phase of the liquid feed 102. Frequently, the precursor will be a material, such as a salt, dissolved in a liquid solvent of the liquid feed 102. The precursor may undergo one or more chemical reactions in the furnace 110 to assist in production of the particles 112. Alternatively, the precursor material may contribute to formation of the particles 112 without undergoing chemical reaction. This could be the case, for example, when the liquid feed 102 includes, as a precursor material, suspended particles that are not chemically modified in the furnace 110. In any event, the particles 112 comprise at least one component originally contributed by the precursor.

The liquid feed 102 may include multiple precursor materials, which may be present together in a single phase or separately in multiple phases. For example, the liquid feed 102 may include multiple precursors in solution in a single liquid vehicle. Alternatively, one precursor material could be in a solid particulate phase and a second precursor material could be in a liquid phase. Also, one precursor material could be in one liquid phase and a second precursor material could be in a second liquid phase, such as could be the case when the liquid feed 102 comprises an emulsion. Different components contributed by different precursors may be present in the particles together in a single material phase, or the different components may be present in different material phases when the particles 112 are composites of multiple phases. Specific examples of preferred precursor materials are discussed more fully below.

The carrier gas 104 may comprise any gaseous medium in which droplets produced from the liquid feed 102 may be dispersed in aerosol form. Also, the carrier gas 104 may be inert, in that the carrier gas 104 does not participate in formation of the particles 112. Alternatively, the carrier gas may have one or more active component(s) that contribute to formation of the particles 112. In that regard, the carrier gas may include one or more reactive components that react in the furnace 110 to contribute to

formation of the particles 112. Preferred carrier gas compositions are discussed more fully below.

The aerosol generator 106 atomizes the liquid feed 102 to form droplets in a manner to permit the carrier gas 104 to sweep the droplets away to form the aerosol 108. The droplets comprise liquid from the liquid feed 102. The droplets may, however, also include nonliquid material, such as one or more small particles held in the droplet by the liquid. For example, when the particles 112 are composite, or multi-phase, particles, one phase of the composite may be provided in the liquid feed 102 in the form of suspended precursor particles and a second phase of the composite may be produced in the furnace 110 from one or more precursors in the liquid phase of the liquid feed 102. Furthermore the precursor particles could be included in the liquid feed 102, and therefore also in droplets of the aerosol 108, for the purpose only of dispersing the particles for subsequent compositional or structural modification during or after processing in the furnace 110.

An important aspect of the present invention is generation of the aerosol 108 with droplets of a small average size, narrow size distribution. In this manner, the particles 112 may be produced at a desired small size with a narrow size distribution, which are advantageous for many applications.

The aerosol generator 106 is capable of producing the aerosol 108 such that it includes droplets having a weight average size in a range having a lower limit of about 1 μm and preferably about 2 μm; and an upper limit of about 10 μm; preferably about 7 μm, more preferably about 5 μm and most preferably about 4 μm. A weight average droplet size in a range of from about 2 μm to about 4 μm is more preferred for most applications, with a weight average droplet size of about 3 μm being particularly preferred for some applications. The aerosol generator is also capable of producing the aerosol 108 such that it includes droplets in a narrow size distribution. Preferably, the droplets in the aerosol are such that at least about 70 percent (more preferably at least about 80 weight percent and most preferably at least about 85 weight percent) of the droplets are smaller than about 10 μm and more preferably at least about 70 weight percent (more preferably at least about 80 weight percent and most preferably at least about 85 weight percent) are smaller than about 5 μm. Furthermore, preferably no greater than about 30 weight percent, more preferably no greater than about 25 weight percent

and most preferably no greater than about 20 weight percent, of the droplets in the aerosol 108 are larger than about twice the weight average droplet size.

Another important aspect of the present invention is that the aerosol 108 may be generated without consuming excessive amounts of the carrier gas 104. The aerosol generator 106 is capable of producing the aerosol 108 such that it has a high loading, or high concentration, of the liquid feed 102 in droplet form. In that regard, the aerosol 108 preferably includes greater than about 1×10^6 droplets per cubic centimeter of the aerosol 108, more preferably greater than about 5×10^6 droplets per cubic centimeter, still more preferably greater than about 1×10^7 droplets per cubic centimeter, and most preferably greater than about 5×10^7 droplets per cubic centimeter. That the aerosol generator 106 can produce such a heavily loaded aerosol 108 is particularly surprising considering the high quality of the aerosol 108 with respect to small average droplet size and narrow droplet size distribution. Typically, droplet loading in the aerosol is such that the volumetric ratio of liquid feed 102 to carrier gas 104 in the aerosol 108 is larger than about 0.04 milliliters of liquid feed 102 per liter of carrier gas 104 in the aerosol 108, preferably larger than about 0.083 milliliters of liquid feed 102 per liter of carrier gas 104 in the aerosol 108, more preferably larger than about 0.167 milliliters of liquid feed 102 per liter of carrier gas 104, still more preferably larger than about 0.25 milliliters of liquid feed 102 per liter of carrier gas 104, and most preferably larger than about 0.333 milliliters of liquid feed 102 per liter of carrier gas 104.

This capability of the aerosol generator 106 to produce a heavily loaded aerosol 108 is even more surprising given the high droplet output rate of which the aerosol generator 106 is capable, as discussed more fully below. It will be appreciated that the concentration of liquid feed 102 in the aerosol 108 will depend upon the specific components and attributes of the liquid feed 102 and, particularly, the size of the droplets in the aerosol 108. For example, when the average droplet size is from about 2 μm to about 4 μm, the droplet loading is preferably larger than about 0.15 milliliters of aerosol feed 102 per liter of carrier gas 104, more preferably larger than about 0.2 milliliters of liquid feed 102 per liter of carrier gas 104, even more preferably larger than about 0.2 milliliters of liquid feed 102 per liter of carrier gas 104, and most preferably larger than about 0.3 milliliters of liquid feed 102 per liter of carrier gas 104. When reference is

made herein to liters of carrier gas 104, it refers to the volume that the carrier gas 104 would occupy under conditions of standard temperature and pressure.

The furnace 110 may be any suitable device for heating the aerosol 108 to evaporate liquid from the droplets of the aerosol 108 and thereby permit formation of the particles 112. The maximum average stream temperature, or reaction temperature, refers to the maximum average temperature that an aerosol stream attains while flowing through the furnace. This is typically determined by a temperature probe inserted into the furnace. Preferred reaction temperatures according to the present invention are discussed more fully below.

Although longer residence times are possible, for many applications, residence time in the heating zone of the furnace 110 of shorter than about 4 seconds is typical, with shorter than about 2 seconds being preferred, shorter than about 1 second being more preferred, shorter than about 0.5 second being even more preferred, and shorter than about 0.2 second being most preferred. The residence time should be long enough, however, to assure that the particles 112 attain the desired maximum stream temperature for a given heat transfer rate. In that regard, with extremely short residence times, higher furnace temperatures could be used to increase the rate of heat transfer so long as the particles 112 attain a maximum temperature within the desired stream temperature range. That mode of operation, however, is not preferred. Also, it is noted that as used herein, residence time refers to the actual time for a material to pass through the relevant process equipment. In the case of the furnace, this includes the effect of increasing velocity with gas expansion due to heating.

Typically, the furnace 110 will be a tube-shaped furnace, so that the aerosol 108 moving into and through the furnace does not encounter sharp edges on which droplets could collect. Loss of droplets to collection at sharp surfaces results in a lower yield of particles 112. More important, however, the accumulation of liquid at sharp edges can result in re-release of undesirably large droplets back into the aerosol 108, which can cause contamination of the particulate product 116 with undesirably large particles. Also, over time, such liquid collection at sharp surfaces can cause fouling of process equipment, impairing process performance.

Also, although the present invention is described with primary reference to a furnace reactor, which is preferred, it should be recognized that, except as noted, any

other thermal reactor, including a flame reactor or a plasma reactor, could be used instead. A furnace reactor is, however, preferred, because of the generally even heating characteristic of a furnace for attaining a uniform stream temperature.

The particle collector 114, may be any suitable apparatus for collecting particles 112 to produce the particulate product 116. One preferred embodiment of the particle collector 114 uses one or more filter to separate the particles 112 from gas. Such a filter may be of any type, including a bag filter. Another preferred embodiment of the particle collector uses one or more cyclone to separate the particles 112. Other apparatus that may be used in the particle collector 114 includes an electrostatic precipitator. Also, collection should normally occur at a temperature above the condensation temperature of the gas stream in which the particles 112 are suspended. Also, collection should normally be at a temperature that is low enough to prevent significant agglomeration of the particles 112.

Of significant importance to the operation of the process of the present invention is the aerosol generator 106, which must be capable of producing a high quality aerosol with high droplet loading, as previously noted. With reference to Fig. 2, one embodiment of an aerosol generator 106 of the present invention is described. The aerosol generator 106 includes a plurality of ultrasonic transducer discs 120 that are each mounted in a transducer housing 122. The transducer housings 122 are mounted to a transducer mounting plate 124, creating an array of the ultrasonic transducer discs 120. Any convenient spacing may be used for the ultrasonic transducer discs 120. Center-to-center spacing of the ultrasonic transducer discs 120 of about 4 centimeters is often adequate. The aerosol generator 106, as shown in Fig. 2, includes forty-nine transducers in a 7 x 7 array. The array configuration is as shown in Fig. 3, which depicts the locations of the transducer housings 122 mounted to the transducer mounting plate 124.

With continued reference to Fig. 2, a separator 126, in spaced relation to the transducer discs 120, is retained between a bottom retaining plate 128 and a top retaining plate 130. Gas delivery tubes 132 are connected to gas distribution manifolds 134, which have gas delivery ports 136. The gas distribution manifolds 134 are housed within a generator body 138 that is covered by generator lid 140. A transducer driver 144, having circuitry for driving the transducer discs 120, is electronically connected with the transducer discs 120 via electrical cables 146.

During operation of the aerosol generator 106, as shown in Fig. 2, the transducer discs 120 are activated by the transducer driver 144 via the electrical cables 146. The transducers preferably vibrate at a frequency of from about 1 MHz to about 5 MHz, more preferably from about 1.5 MHz to about 3 MHz. Frequently used frequencies are at about 1.6 MHz and about 2.4 MHz. Furthermore, all of the transducer discs 110 should be operating at substantially the same frequency when an aerosol with a narrow droplet size distribution is desired. This is important because commercially available transducers can vary significantly in thickness, sometimes by as much as 10%. It is preferred, however, that the transducer discs 120 operate at frequencies within a range of 5% above and below the median transducer frequency, more preferably within a range of 2.5%, and most preferably within a range of 1%. This can be accomplished by careful selection of the transducer discs 120 so that they all preferably have thicknesses within 5% of the median transducer thickness, more preferably within 2.5%, and most preferably within 1%.

Liquid feed 102 enters through a feed inlet 148 and flows through flow channels 150 to exit through feed outlet 152. An ultrasonically transmissive fluid, typically water, enters through a water inlet 154 to fill a water bath volume 156 and flow through flow channels 158 to exit through a water outlet 160. A proper flow rate of the ultrasonically transmissive fluid is necessary to cool the transducer discs 120 and to prevent overheating of the ultrasonically transmissive fluid. Ultrasonic signals from the transducer discs 120 are transmitted, via the ultrasonically transmissive fluid, across the water bath volume 156, and ultimately across the separator 126, to the liquid feed 102 in flow channels 150.

The ultrasonic signals from the ultrasonic transducer discs 120 cause atomization cones 162 to develop in the liquid feed 102 at locations corresponding with the transducer discs 120. Carrier gas 104 is introduced into the gas delivery tubes 132 and delivered to the vicinity of the atomization cones 162 via gas delivery ports 136. Jets of carrier gas exit the gas delivery ports 136 in a direction so as to impinge on the atomization cones 162, thereby sweeping away atomized droplets of the liquid feed 102 that are being generated from the atomization cones 162 and creating the aerosol 108, which exits the aerosol generator 106 through an aerosol exit opening 164.

Efficient use of the carrier gas 104 is an important aspect of the aerosol generator 106. The embodiment of the aerosol generator 106 shown in Fig. 2 includes two gas exit ports per atomization cone 162, with the gas ports being positioned above the liquid medium 102 over troughs that develop between the atomization cones 162, such that the exiting carrier gas 104 is horizontally directed at the surface of the atomization cones 162, thereby efficiently distributing the carrier gas 104 to critical portions of the liquid feed 102 for effective and efficient sweeping away of droplets as they form about the ultrasonically energized atomization cones 162. Furthermore, it is preferred that at least a portion of the opening of each of the gas delivery ports 136, through which the carrier gas exits the gas delivery tubes, should be located below the top of the atomization cones 162 at which the carrier gas 104 is directed. This relative placement of the gas delivery ports 136 is very important to efficient use of carrier gas 104. Orientation of the gas delivery ports 136 is also important. Preferably, the gas delivery ports 136 are positioned to horizontally direct jets of the carrier gas 104 at the atomization cones 162. The aerosol generator 106 permits generation of the aerosol 108 with heavy loading with droplets of the carrier liquid 102, unlike aerosol generator designs that do not efficiently focus gas delivery to the locations of droplet formation.

Another important feature of the aerosol generator 106, as shown in Fig. 2, is the use of the separator 126, which protects the transducer discs 120 from direct contact with the liquid feed 102, which is often highly corrosive. The height of the separator 126 above the top of the transducer discs 120 should normally be kept as small as possible, and is often in the range of from about 1 centimeter to about 2 centimeters. The top of the liquid feed 102 in the flow channels above the tops of the ultrasonic transducer discs 120 is typically in a range of from about 2 centimeters to about 5 centimeters, whether or not the aerosol generator includes the separator 126, with a distance of about 3 to 4 centimeters being preferred. Although the aerosol generator 106 could be made without the separator 126, in which case the liquid feed 102 would be in direct contact with the transducer discs 120, the highly corrosive nature of the liquid feed 102 can often cause premature failure of the transducer discs 120. The use of the separator 126, in combination with use of the ultrasonically transmissive fluid in the water bath volume 156 to provide ultrasonic coupling, significantly extending the life of the ultrasonic transducers 120. One disadvantage of using the separator 126, however, is that the rate

of droplet production from the atomization cones 162 is reduced, often by a factor of two or more, relative to designs in which the liquid feed 102 is in direct contact with the ultrasonic transducer discs 102. Even with the separator 126, however, the aerosol generator 106 used with the present invention is capable of producing a high quality aerosol with heavy droplet loading, as previously discussed. Suitable materials for the separator 126 include, for example, polyamides (such as Kapton™ membranes from DuPont) and other polymer materials, glass, and plexiglass. The main requirements for the separator 126 are that it be ultrasonically transmissive, corrosion resistant and impermeable.

One alternative to using the separator 126 is to bind a corrosion-resistant protective coating onto the surface of the ultrasonic transducer discs 120, thereby preventing the liquid feed 102 from contacting the surface of the ultrasonic transducer discs 120. When the ultrasonic transducer discs 120 have a protective coating, the aerosol generator 106 will typically be constructed without the water bath volume 156 and the liquid feed 102 will flow directly over the ultrasonic transducer discs 120. Examples of such protective coating materials include platinum, gold, TEFLON™, epoxies and various plastics. Such coating typically significantly extends transducer life. Also, when operating without the separator 126, the aerosol generator 106 will typically produce the aerosol 108 with a much higher droplet loading than when the separator 126 is used.

The design for the aerosol generator 106 based on an array of ultrasonic transducers is versatile and is easily modified to accommodate different generator sizes for different specialty applications. The aerosol generator 106 may be designed to include a plurality of ultrasonic transducers in any convenient number. Even for smaller scale production, however, the aerosol generator 106 preferably has at least nine ultrasonic transducers, more preferably at least 16 ultrasonic transducers, and even more preferably at least 25 ultrasonic transducers. For larger scale production, however, the aerosol generator 106 includes at least 40 ultrasonic transducers, more preferably at least 100 ultrasonic transducers, and even more preferably at least 400 ultrasonic transducers. In some large volume applications, the aerosol generator may have at least 1000 ultrasonic transducers.

Figs. 4-21 show component designs for an aerosol generator 106 including an array of 400 ultrasonic transducers. Referring first to Figs. 4 and 5, the transducer mounting plate 124 is shown with a design to accommodate an array of 400 ultrasonic transducers, arranged in four subarrays of 100 ultrasonic transducers each. The transducer mounting plate 124 has integral vertical walls 172 for containing the ultrasonically transmissive fluid, typically water, in a water bath similar to the water bath volume 156 described previously with reference to Fig. 5.

As shown in Figs. 4 and 5, four hundred transducer mounting receptacles 174 are provided in the transducer mounting plate 124 for mounting ultrasonic transducers for the desired array. With reference to Fig. 6, the profile of an individual transducer mounting receptacle 174 is shown. A mounting seat 176 accepts an ultrasonic transducer for mounting, with a mounted ultrasonic transducer being held in place via screw holes 178. Opposite the mounting receptacle 176 is a flared opening 180 through which an ultrasonic signal may be transmitted for the purpose of generating the aerosol 108, as previously described with reference to Fig. 2.

A preferred transducer mounting configuration, however, is shown in Fig. 7 for another configuration for the transducer mounting plate 124. As seen in Fig. 7, an ultrasonic transducer disc 120 is mounted to the transducer mounting plate 124 by use of a compression screw 177 threaded into a threaded receptacle 179. The compression screw 177 bears against the ultrasonic transducer disc 120, causing an o-ring 181, situated in an o-ring seat 182 on the transducer mounting plate, to be compressed to form a seal between the transducer mounting plate 124 and the ultrasonic transducer disc 120. This type of transducer mounting is particularly preferred when the ultrasonic transducer disc 120 includes a protective surface coating, as discussed previously, because the seal of the o-ring to the ultrasonic transducer disc 120 will be inside of the outer edge of the protective seal, thereby preventing liquid from penetrating under the protective surface coating from the edges of the ultrasonic transducer disc 120.

Referring now to Fig. 11, the bottom retaining plate 128 for a 400 transducer array is shown having a design for mating with the transducer mounting plate 124 (shown in Figs. 4-5). The bottom retaining plate 128 has eighty openings 184, arranged in four subgroups 186 of twenty openings 184 each. Each of the openings 184 corresponds with five of the transducer mounting receptacles 174 (shown in Figs. 4 and 5) when the bottom

retaining plate 128 is mated with the transducer mounting plate 124 to create a volume for a water bath between the transducer mounting plate 124 and the bottom retaining plate 128. The openings 184, therefore, provide a pathway for ultrasonic signals generated by ultrasonic transducers to be transmitted through the bottom retaining plate.

Referring now to Figs. 9 and 10, a liquid feed box 190 for a 400 transducer array is shown having the top retaining plate 130 designed to fit over the bottom retaining plate 128 (shown in Fig. 8), with a separator 126 (not shown) being retained between the bottom retaining plate 128 and the top retaining plate 130 when the aerosol generator 106 is assembled. The liquid feed box 190 also includes vertically extending walls 192 for containing the liquid feed 102 when the aerosol generator is in operation. Also shown in Figs. 9 and 10 is the feed inlet 148 and the feed outlet 152. An adjustable weir 198 determines the level of liquid feed 102 in the liquid feed box 190 during operation of the aerosol generator 106.

The top retaining plate 130 of the liquid feed box 190 has eighty openings 194 therethrough, which are arranged in four subgroups 196 of twenty openings 194 each. The openings 194 of the top retaining plate 130 correspond in size with the openings 184 of the bottom retaining plate 128 (shown in Fig. 8). When the aerosol generator 106 is assembled, the openings 194 through the top retaining plate 130 and the openings 184 through the bottom retaining plate 128 are aligned, with the separator 126 positioned therebetween, to permit transmission of ultrasonic signals when the aerosol generator 106 is in operation.

Referring now to Figs. 9-11, a plurality of gas tube feed-through holes 202 extend through the vertically extending walls 192 to either side of the assembly including the feed inlet 148 and feed outlet 152 of the liquid feed box 190. The gas tube feed-through holes 202 are designed to permit insertion therethrough of gas tubes 208 of a design as shown in Fig. 14. When the aerosol generator 106 is assembled, a gas tube 208 is inserted through each of the gas tube feed-through holes 202 so that gas delivery ports 136 in the gas tube 208 will be properly positioned and aligned adjacent the openings 194 in the top retaining plate 130 for delivery of gas to atomization cones that develop in the liquid feed box 190 during operation of the aerosol generator 106. The gas delivery ports 136 are typically holes having a diameter of from about 1.5 millimeters to about 3.5 millimeters.

Referring now to Fig. 12, a partial view of the liquid feed box 190 is shown with gas tubes 208A, 208B and 208C positioned adjacent to the openings 194 through the top retaining plate 130. Also shown in Fig. 12 are the relative locations that ultrasonic transducer discs 120 would occupy when the aerosol generator 106 is assembled. As seen in Fig. 12, the gas tube 208A, which is at the edge of the array, has five gas delivery ports 136. Each of the gas delivery ports 136 is positioned to divert carrier gas 104 to a different one of atomization cones that develop over the array of ultrasonic transducer discs 120 when the aerosol generator 106 is operating. The gas tube 208B, which is one row in from the edge of the array, is a shorter tube that has ten gas delivery ports 136, five each on opposing sides of the gas tube 208B. The gas tube 208B, therefore, has gas delivery ports 136 for delivering gas to atomization cones corresponding with each of ten ultrasonic transducer discs 120. The third gas tube, 208C, is a longer tube that also has ten gas delivery ports 136 for delivering gas to atomization cones corresponding with ten ultrasonic transducer discs 120. The design shown in Fig. 12, therefore, includes one gas delivery port per ultrasonic transducer disc 120. Although this is a lower density of gas delivery ports 136 than for the embodiment of the aerosol generator 106 shown in Fig. 2, which includes two gas delivery ports per ultrasonic transducer disc 120, the design shown in Fig. 12 is, nevertheless, capable of producing a dense, high-quality aerosol without unnecessary waste of gas.

Referring now to Fig. 13, the flow of carrier gas 104 relative to atomization cones 162 during operation of the aerosol generator 106 having a gas distribution configuration to deliver carrier gas 104 from gas delivery ports on both sides of the gas tubes 208, as was shown for the gas tubes 208A, 208B and 208C in the gas distribution configuration shown in Fig. 11. The carrier gas 104 sweeps both directions from each of the gas tubes 208.

An alternative, and preferred, flow for carrier gas 104 is shown in Fig. 14. As shown in Fig. 14, carrier gas 104 is delivered from only one side of each of the gas tubes 208. This results in a sweep of carrier gas from all of the gas tubes 208 toward a central area 212. This results in a more uniform flow pattern for aerosol generation that may significantly enhance the efficiency with which the carrier gas 104 is used to produce an aerosol. The aerosol that is generated, therefore, tends to be more heavily loaded with liquid droplets.

Another configuration for distributing carrier gas in the aerosol generator 106 is shown in Figs. 15 and 16. In this configuration, the gas tubes 208 are hung from a gas distribution plate 216 adjacent gas flow holes 218 through the gas distribution plate 216. In the aerosol generator 106, the gas distribution plate 216 would be mounted above the liquid feed, with the gas flow holes positioned to each correspond with an underlying ultrasonic transducer. Referring specifically to Fig. 16, when the ultrasonic generator 106 is in operation, atomization cones 162 develop through the gas flow holes 218, and the gas tubes 208 are located such that carrier gas 104 exiting from ports in the gas tubes 208 impinge on the atomization cones and flow upward through the gas flow holes. The gas flow holes 218, therefore, act to assist in efficiently distributing the carrier gas 104 about the atomization cones 162 for aerosol formation. It should be appreciated that the gas distribution plates 218 can be made to accommodate any number of the gas tubes 208 and gas flow holes 218. For convenience of illustration, the embodiment shown in Figs. 15 and 16 shows a design having only two of the gas tubes 208 and only 16 of the gas flow holes 218. Also, it should be appreciated that the gas distribution plate 216 could be used alone, without the gas tubes 208. In that case, a slight positive pressure of carrier gas 104 would be maintained under the gas distribution plate 216 and the gas flow holes 218 would be sized to maintain the proper velocity of carrier gas 104 through the gas flow holes 218 for efficient aerosol generation. Because of the relative complexity of operating in that mode, however, it is not preferred.

Aerosol generation may also be enhanced through mounting of ultrasonic transducers at a slight angle and directing the carrier gas at resulting atomization cones such that the atomization cones are tilting in the same direction as the direction of flow of carrier gas. Referring to Fig. 17, an ultrasonic transducer disc 120 is shown. The ultrasonic transducer disc 120 is tilted at a tilt angle 114 (typically less than 10 degrees), so that the atomization cone 162 will also have a tilt. It is preferred that the direction of flow of the carrier gas 104 directed at the atomization cone 162 is in the same direction as the tilt of the atomization cone 162.

Referring now to Figs. 18 and 19, a gas manifold 220 is shown for distributing gas to the gas tubes 208 in a 400 transducer array design. The gas manifold 220 includes a gas distribution box 222 and piping stubs 224 for connection with gas tubes 208 (shown in Fig. 11). Inside the gas distribution box 222 are two gas distribution plates 226 that

form a flow path to assist in distributing the gas equally throughout the gas distribution box 222, to promote substantially equal delivery of gas through the piping stubs 224. The gas manifold 220, as shown in Figs. 18 and 19, is designed to feed eleven gas tubes 208. For the 400 transducer design, a total of four gas manifolds 220 are required.

Referring now to Figs. 20 and 21, the generator lid 140 is shown for a 400 transducer array design. The generator lid 140 mates with and covers the liquid feed box 190 (shown in Figs. 9 and 10). The generator lid 140, as shown in Figs. 20 and 21, has a hood design to permit easy collection of the aerosol 108 without subjecting droplets in the aerosol 108 to sharp edges on which droplets may coalesce and be lost, and possibly interfere with the proper operation of the aerosol generator 106. When the aerosol generator 106 is in operation, the aerosol 108 would be withdrawn via the aerosol exit opening 164 through the generator cover 140.

Although the aerosol generator 106 produces a high quality aerosol 108 having a high droplet loading, it is often desirable to further concentrate the aerosol 108 prior to introduction into the furnace 110. Referring now to Fig. 22, a process flow diagram is shown for one embodiment of the present invention involving such concentration of the aerosol 108. As shown in Fig. 22, the aerosol 108 from the aerosol generator 106 is sent to an aerosol concentrator 236 where excess carrier gas 238 is withdrawn from the aerosol 108 to produce a concentrated aerosol 240, which is then fed to the furnace 110.

The aerosol concentrator 236 typically includes one or more virtual impactors capable of concentrating droplets in the aerosol 108 by a factor of greater than about 2, preferably by a factor of greater than about 5, and more preferably by a factor of greater than about 10, to produce the concentrated aerosol 240. According to the present invention, the concentrated aerosol 240 should typically contain greater than about 1×10^7 droplets per cubic centimeter, and more preferably from about 5×10^7 to about 5×10^8 droplets per cubic centimeter. A concentration of about 1×10^8 droplets per cubic centimeter of the concentrated aerosol is particularly preferred, because when the concentrated aerosol 240 is loaded more heavily than that, then the frequency of collisions between droplets becomes large enough to impair the properties of the concentrated aerosol 240, resulting in potential contamination of the particulate product 116 with an undesirably large quantity of over-sized particles. For example, if the aerosol 108 has a concentration of about 1×10^7 droplets per cubic centimeter, and the aerosol

concentrator 236 concentrates droplets by a factor of 10, then the concentrated aerosol 240 will have a concentration of about 1 x 10^8 droplets per cubic centimeter. Stated another way, for example, when the aerosol generator generates the aerosol 108 with a droplet loading of about 0.167 milliliters liquid feed 102 per liter of carrier gas 104, the concentrated aerosol 240 would be loaded with about 1.67 milliliters of liquid feed 102 per liter of carrier gas 104, assuming the aerosol 108 is concentrated by a factor of 10.

Having a high droplet loading in aerosol feed to the furnace provides the important advantage of reducing the heating demand on the furnace 110 and the size of flow conduits required through the furnace. Also, other advantages of having a dense aerosol include a reduction in the demands on cooling and particle collection components, permitting significant equipment and operational savings. Furthermore, as system components are reduced in size, powder holdup within the system is reduced, which is also desirable. Concentration of the aerosol stream prior to entry into the furnace 110, therefore, provides a substantial advantage relative to processes that utilize less concentrated aerosol streams.

The excess carrier gas 238 that is removed in the aerosol concentrator 236 typically includes extremely small droplets that are also removed from the aerosol 108. Preferably, the droplets removed with the excess carrier gas 238 have a weight average size of smaller than about 1.5 μm, and more preferably smaller than about 1 μm and the droplets retained in the concentrated aerosol 240 have an average droplet size of larger than about 2 μm. For example, a virtual impactor sized to treat an aerosol stream having a weight average droplet size of about three μm might be designed to remove with the excess carrier gas 238 most droplets smaller than about 1.5 μm in size. Other designs are also possible. When using the aerosol generator 106 with the present invention, however, the loss of these very small droplets in the aerosol concentrator 236 will typically constitute no more than about 10 percent by weight, and more preferably no more than about 5 percent by weight, of the droplets originally in the aerosol stream that is fed to the concentrator 236. Although the aerosol concentrator 236 is useful in some situations, it is normally not required with the process of the present invention, because the aerosol generator 106 is capable, in most circumstances, of generating an aerosol stream that is sufficiently dense. So long as the aerosol stream coming out of the aerosol generator 102 is sufficiently dense, it is preferred that the aerosol concentrator not be used. It is a

significant advantage of the present invention that the aerosol generator 106 normally generates such a dense aerosol stream that the aerosol concentrator 236 is not needed. Therefore, the complexity of operation of the aerosol concentrator 236 and accompanying liquid losses may typically be avoided.

It is important that the aerosol stream (whether it has been concentrated or not) that is fed to the furnace 110 have a high droplet flow rate and high droplet loading as would be required for most industrial applications. With the present invention, the aerosol stream fed to the furnace preferably includes a droplet flow of greater than about 0.5 liters per hour, more preferably greater than about 2 liters per hour, still more preferably greater than about 5 liters per hour, even more preferably greater than about 10 liters per hour, particularly greater than about 50 liters per hour and most preferably greater than about 100 liters per hour; and with the droplet loading being typically greater than about 0.04 milliliters of droplets per liter of carrier gas, preferably greater than about 0.083 milliliters of droplets per liter of carrier gas 104, more preferably greater than about 0.167 milliliters of droplets per liter of carrier gas 104, still more preferably greater than about 0.25 milliliters of droplets per liter of carrier gas 104, particularly greater than about 0.33 milliliters of droplets per liter of carrier gas 104 and most preferably greater than about 0.83 milliliters of droplets per liter of carrier gas 104.

One embodiment of a virtual impactor that could be used as the aerosol concentrator 236 will now be described with reference to Figs. 23-29. A virtual impactor 246 includes an upstream plate assembly 248 (details shown in Figs. 24-26) and a downstream plate assembly 250 (details shown in Figs. 21-39), with a concentrating chamber 262 located between the upstream plate assembly 248 and the downstream plate assembly 250.

Through the upstream plate assembly 248 are a plurality of vertically extending inlet slits 254. The downstream plate assembly 250 includes a plurality of vertically extending exit slits 256 that are in alignment with the inlet slits 254. The exit slits 256 are, however, slightly wider than the inlet slits 254. The downstream plate assembly 250 also includes flow channels 258 that extend substantially across the width of the entire downstream plate assembly 250, with each flow channel 258 being adjacent to an excess gas withdrawal port 260.

During operation, the aerosol 108 passes through the inlet slits 254 and into the concentrating chamber 262. Excess carrier gas 238 is withdrawn from the concentrating chamber 262 via the excess gas withdrawal ports 260. The withdrawn excess carrier gas 238 then exits via a gas duct port 264. That portion of the aerosol 108 that is not withdrawn through the excess gas withdrawal ports 260 passes through the exit slits 256 and the flow channels 258 to form the concentrated aerosol 240. Those droplets passing across the concentrating chamber 262 and through the exit slits 256 are those droplets of a large enough size to have sufficient momentum to resist being withdrawn with the excess carrier gas 238.

As seen best in Figs. 24-29, the inlet slits 254 of the upstream plate assembly 248 include inlet nozzle extension portions 266 that extend outward from the plate surface 268 of the upstream plate assembly 248. The exit slits 256 of the downstream plate assembly 250 include exit nozzle extension portions 270 extending outward from a plate surface 272 of the downstream plate assembly 250. These nozzle extension portions 266 and 270 are important for operation of the virtual impactor 246, because having these nozzle extension portions 266 and 270 permits a very close spacing to be attained between the inlet slits 254 and the exit slits 256 across the concentrating chamber 262, while also providing a relatively large space in the concentrating chamber 262 to facilitate efficient removal of the excess carrier gas 238.

Also as best seen in Figs. 24-29, the inlet slits 254 have widths that flare outward toward the side of the upstream plate assembly 248 that is first encountered by the aerosol 108 during operation. This flared configuration reduces the sharpness of surfaces encountered by the aerosol 108, reducing the loss of aerosol droplets and potential interference from liquid buildup that could occur if sharp surfaces were present. Likewise, the exit slits 256 have a width that flares outward towards the flow channels 258, thereby allowing the concentrated aerosol 240 to expand into the flow channels 258 without encountering sharp edges that could cause problems.

As noted previously, both the inlet slits 254 of the upstream plate assembly 248 and the exit slits 256 of the downstream plate assembly 250 are vertically extending. This configuration is advantageous for permitting liquid that may collect around the inlet slits 254 and the exit slits 256 to drain away. The inlet slits 254 and the exit slits 256 need not, however, have a perfectly vertical orientation. Rather, it is often desirable to

slant the slits backward (sloping upward and away in the direction of flow) by about five to ten degrees relative to vertical, to enhance draining of liquid off of the upstream plate assembly 248 and the downstream plate assembly 250. This drainage function of the vertically extending configuration of the inlet slits 254 and the outlet slits 256 also inhibits liquid build-up in the vicinity of the inlet slits 248 and the exit slits 250, which liquid build-up could result in the release of undesirably large droplets into the concentrated aerosol 240.

As discussed previously, the aerosol generator 106 of the present invention produces a concentrated, high quality aerosol of micro-sized droplets having a relatively narrow size distribution. It has been found, however, that for many applications the process of the present invention is significantly enhanced by further classifying by size the droplets in the aerosol 108 prior to introduction of the droplets into the furnace 110. In this manner, the size and size distribution of particles in the particulate product 116 are further controlled.

Referring now to Fig. 30, a process flow diagram is shown for one embodiment of the process of the present invention including such droplet classification. As shown in Fig. 30, the aerosol 108 from the aerosol generator 106 goes to a droplet classifier 280 where oversized droplets are removed from the aerosol 108 to prepare a classified aerosol 282. Liquid 284 from the oversized droplets that are being removed is drained from the droplet classifier 280. This drained liquid 284 may advantageously be recycled for use in preparing additional liquid feed 102.

Any suitable droplet classifier may be used for removing droplets above a predetermined size. For example, a cyclone could be used to remove over-size droplets. A preferred droplet classifier for many applications, however, is an impactor. One embodiment of an impactor for use with the present invention will now be described with reference to Figs. 31-35.

As seen in Fig. 31, an impactor 288 has disposed in a flow conduit 286 a flow control plate 290 and an impactor plate assembly 292. The flow control plate 290 is conveniently mounted on a mounting plate 294.

The flow control plate 290 is used to channel the flow of the aerosol stream toward the impactor plate assembly 292 in a manner with controlled flow characteristics that are desirable for proper impaction of oversize droplets on the impactor plate

assembly 292 for removal through the drains 296 and 314. One embodiment of the flow control plate 290 is shown in Fig. 32. The flow control plate 290 has an array of circular flow ports 296 for channeling flow of the aerosol 108 towards the impactor plate assembly 292 with the desired flow characteristics.

Details of the mounting plate 294 are shown in Fig. 33. The mounting plate 294 has a mounting flange 298 with a large diameter flow opening 300 passing therethrough to permit access of the aerosol 108 to the flow ports 296 of the flow control plate 290 (shown in Fig. 32).

Referring now to Figs. 34 and 35, one embodiment of an impactor plate assembly 292 is shown. The impactor plate assembly 292 includes an impactor plate 302 and mounting brackets 304 and 306 used to mount the impactor plate 302 inside of the flow conduit 286. The impactor plate 302 and the flow channel plate 290 are designed so that droplets larger than a predetermined size will have momentum that is too large for those particles to change flow direction to navigate around the impactor plate 302.

During operation of the impactor 288, the aerosol 108 from the aerosol generator 106 passes through the upstream flow control plate 290. Most of the droplets in the aerosol navigate around the impactor plate 302 and exit the impactor 288 through the downstream flow control plate 290 in the classified aerosol 282. Droplets in the aerosol 108 that are too large to navigate around the impactor plate 302 will impact on the impactor plate 302 and drain through the drain 296 to be collected with the drained liquid 284 (as shown in Fig. 31).

The configuration of the impactor plate 302 shown in Fig. 30 represents only one of many possible configurations for the impactor plate 302. For example, the impactor 288 could include an upstream flow control plate 290 having vertically extending flow slits therethrough that are offset from vertically extending flow slits through the impactor plate 302, such that droplets too large to navigate the change in flow due to the offset of the flow slits between the flow control plate 290 and the impactor plate 302 would impact on the impactor plate 302 to be drained away. Other designs are also possible.

In a preferred embodiment of the present invention, the droplet classifier 280 is typically designed to remove droplets from the aerosol 108 that are larger than about 15 μm in size, more preferably to remove droplets larger than about 10 μm in size, even more preferably to remove droplets of a size larger than about 8 μm in size and most

preferably to remove droplets larger than about 5 μm in size. The droplet classification size in the droplet classifier is preferably smaller than about 15 μm, more preferably smaller than about 10 μm, even more preferably smaller than about 8 μm and most preferably smaller than about 5 μm. The classification size, also called the classification cut point, is that size at which half of the droplets of that size are removed and half of the droplets of that size are retained. Depending upon the specific application, however, the droplet classification size may be varied, such as by changing the spacing between the impactor plate 302 and the flow control plate 290 or increasing or decreasing aerosol velocity through the jets in the flow control plate 290. Because the aerosol generator 106 of the present invention initially produces a high quality aerosol 108, having a relatively narrow size distribution of droplets, typically less than about 30 weight percent of liquid feed 102 in the aerosol 108 is removed as the drain liquid 284 in the droplet classifier 288, with preferably less than about 25 weight percent being removed, even more preferably less than about 20 weight percent being removed and most preferably less than about 15 weight percent being removed. Minimizing the removal of liquid feed 102 from the aerosol 108 is particularly important for commercial applications to increase the yield of high quality particulate product 116. It should be noted, however, that because of the superior performance of the aerosol generator 106, it is frequently not required to use an impactor or other droplet classifier to obtain a desired absence of oversize droplets to the furnace. This is a major advantage, because the added complexity and liquid losses accompanying use of an impactor may often be avoided with the process of the present invention.

Sometimes it is desirable to use both the aerosol concentrator 236 and the droplet classifier 280 to produce an extremely high quality aerosol stream for introduction into the furnace for the production of particles of highly controlled size and size distribution. Referring now to Fig. 36, one embodiment of the present invention is shown incorporating both the virtual impactor 246 and the impactor 288. Basic components of the virtual impactor 246 and the impactor 288, as shown in Fig. 36, are substantially as previously described with reference to Figs. 26-38. As seen in Fig. 36, the aerosol 108 from the aerosol generator 106 is fed to the virtual impactor 246 where the aerosol stream is concentrated to produce the concentrated aerosol 240. The concentrated aerosol 240 is then fed to the impactor 288 to remove large droplets therefrom and produce the

classified aerosol 282, which may then be fed to the furnace 110. Also, it should be noted that by using both a virtual impactor and an impactor, both undesirably large and undesirably small droplets are removed, thereby producing a classified aerosol with a very narrow droplet size distribution. Also, the order of the aerosol concentrator and the aerosol classifier could be reversed, so that the aerosol concentrator 236 follows the aerosol classifier 280.

One important feature of the design shown in Fig. 36 is the incorporation of drains 310, 312, 314, 316 and 296 at strategic locations. These drains are extremely important for industrial-scale particle production because buildup of liquid in the process equipment can significantly impair the quality of the particulate product 116 that is produced. In that regard, drain 310 drains liquid away from the inlet side of the first plate assembly 248 of the virtual impactor 246. Drain 312 drains liquid away from the inside of the concentrating chamber 262 in the virtual impactor 246 and drain 314 removes liquid that deposits out of the excess carrier gas 238. Drain 316 removes liquid from the vicinity of the inlet side of the flow control plate 290 of the impactor, while the drain 296 removes liquid from the vicinity of the impactor plate 302. Without these drains 310, 312, 314, 316 and 296, the performance of the apparatus shown in Fig. 36 would be significantly impaired. All liquids drained in the drains 310, 312, 314, 316 and 296 may advantageously be recycled for use to prepare the liquid feed 102.

With some applications of the process of the present invention, it may be possible to collect the particles 112 directly from the output of the furnace 110. More often, however, it will be desirable to cool the particles 112 exiting the furnace 110 prior to collection of the particles 112 in the particle collector 114. Referring now to Fig. 37, one embodiment of the process of the present invention is shown in which the particles 112 exiting the furnace 110 are sent to a particle cooler 320 to produce a cooled particle stream 322, which is then feed to the particle collector 114. Although the particle cooler 320 may be any cooling apparatus capable of cooling the particles 112 to the desired temperature for introduction into the particle collector 114, traditional heat exchanger designs are not preferred. This is because a traditional heat exchanger design ordinarily directly subjects the aerosol stream, in which the hot particles 112 are suspended, to cool surfaces. In that situation, significant losses of the particles 112 occur due to thermophoretic deposition of the hot particles 112 on the cool surfaces of the heat

exchanger. According to the present invention, a gas quench apparatus is provided for use as the particle cooler 320 that significantly reduces thermophoretic losses compared to a traditional heat exchanger.

Referring now to Figs. 38-40, one embodiment of a gas quench cooler 330 is shown. The gas quench cooler includes a perforated conduit 332 housed inside of a cooler housing 334 with an annular space 336 located between the cooler housing 334 and the perforated conduit 332. In fluid communication with the annular space 336 is a quench gas inlet box 338, inside of which is disposed a portion of an aerosol outlet conduit 340. The perforated conduit 332 extends between the aerosol outlet conduit 340 and an aerosol inlet conduit 342. Attached to an opening into the quench gas inlet box 338 are two quench gas feed tubes 344. Referring specifically to Fig. 40, the perforated tube 332 is shown. The perforated tube 332 has a plurality of openings 345. The openings 345, when the perforated conduit 332 is assembled into the gas quench cooler 330, permit the flow of quench gas 346 from the annular space 336 into the interior space 348 of the perforated conduit 332. Although the openings 345 are shown as being round holes, any shape of opening could be used, such as slits. Also, the perforated conduit 332 could be a porous screen. Two heat radiation shields 347 prevent downstream radiant heating from the furnace. In most instances, however, it will not be necessary to include the heat radiation shields 347, because downstream radiant heating from the furnace is normally not a significant problem. Use of the heat radiation shields 347 is not preferred due to particulate losses that accompany their use.

With continued reference to Figs. 38-40, operation of the gas quench cooler 330 will now be described. During operation, the particles 112, carried by and dispersed in a gas stream, enter the gas quench cooler 330 through the aerosol inlet conduit 342 and flow into the interior space 348 of perforated conduit 332. Quench gas 346 is introduced through the quench gas feed tubes 344 into the quench gas inlet box 338. Quench gas 346 entering the quench gas inlet box 338 encounters the outer surface of the aerosol outlet conduit 340, forcing the quench gas 346 to flow, in a spiraling, swirling manner, into the annular space 336, where the quench gas 346 flows through the openings 345 through the walls of the perforated conduit 332. Preferably, the gas 346 retains some swirling motion even after passing into the interior space 348. In this way, the particles 112 are quickly cooled with low losses of particles to the walls of the gas quench cooler

330. In this manner, the quench gas 346 enters in a radial direction into the interior space 348 of the perforated conduit 332 around the entire periphery, or circumference, of the perforated conduit 332 and over the entire length of the perforated conduit 332. The cool quench gas 346 mixes with and cools the hot particles 112, which then exit through the aerosol outlet conduit 340 as the cooled particle stream 322. The cooled particle stream 322 can then be sent to the particle collector 114 for particle collection. The temperature of the cooled particle stream 322 is controlled by introducing more or less quench gas. Also, as shown in Fig. 38, the quench gas 346 is fed into the quench cooler 330 in counter flow to flow of the particles. Alternatively, the quench cooler could be designed so that the quench gas 346 is fed into the quench cooler in concurrent flow with the flow of the particles 112. The amount of quench gas 346 fed to the gas quench cooler 330 will depend upon the specific material being made and the specific operating conditions. The quantity of quench gas 346 used, however, must be sufficient to reduce the temperature of the aerosol steam including the particles 112 to the desired temperature. Typically, the particles 112 are cooled to a temperature at least below about 200°C, and often lower. The only limitation on how much the particles 112 are cooled is that the cooled particle stream 322 must be at a temperature that is above the condensation temperature for water as another condensible vapor in the stream. The temperature of the cooled particle stream 322 is often at a temperature of from about 50°C to about 120°C.

Because of the entry of quench gas 346 into the interior space 348 of the perforated conduit 322 in a radial direction about the entire circumference and length of the perforated conduit 322, a buffer of the cool quench gas 346 is formed about the inner wall of the perforated conduit 332, thereby significantly inhibiting the loss of hot particles 112 due to thermophoretic deposition on the cool wall of the perforated conduit 332. In operation, the quench gas 346 exiting the openings 345 and entering into the interior space 348 should have a radial velocity (velocity inward toward the center of the circular cross-section of the perforated conduit 332) of larger than the thermophoretic velocity of the particles 112 inside the perforated conduit 332 in a direction radially outward toward the perforated wall of the perforated conduit 332.

As seen in Figs. 38-40, the gas quench cooler 330 includes a flow path for the particles 112 through the gas quench cooler of a substantially constant cross-sectional shape and area. Preferably, the flow path through the gas quench cooler 330 will have

the same cross-sectional shape and area as the flow path through the furnace 110 and through the conduit delivering the aerosol 108 from the aerosol generator 106 to the furnace 110. Also, particle cooling in the quench cooler is accomplished very quickly, reducing the potential for thermophoretic losses during cooling. The total residence time for aerosol flowing through both the heated zone of the furnace 110 and through the quench cooler is typically shorter than about 5 seconds, more preferably shorter than about 3 seconds, even more preferably shorter than about 2 seconds and most preferably shorter than about 1 second.

In an additional embodiment, the process of the present invention can also incorporate compositional modification of the particles 112 exiting the furnace. Most commonly, the compositional modification will involve forming on the particles 112 a material phase that is different than that of the particles 112, such as by coating the particles 112 with a coating material. One embodiment of the process of the present invention incorporating particle coating is shown in Fig. 41. As shown in Fig. 41, the particles 112 exiting from the furnace 110 go to a particle coater 350 where a coating is placed over the outer surface of the particles 112 to form coated particles 352, which are then sent to the particle collector 114 for preparation of the particulate product 116. Coating methodologies employed in the particle coater 350 are discussed in more detail below.

With continued reference primarily to Fig. 41, in a preferred embodiment, when the particles 112 are coated according to the process of the present invention, the particles 112 are also manufactured via the aerosol process of the present invention, as previously described. The process of the present invention can, however, be used to coat particles that have been premanufactured by a different process, such as by a liquid precipitation route. When coating particles that have been premanufactured by a different route, such as by liquid precipitation, it is preferred that the particles remain in a dispersed state from the time of manufacture to the time that the particles are introduced in slurry form into the aerosol generator 106 for preparation of the aerosol 108 to form the dry particles 112 in the furnace 110, which particles 112 can then be coated in the particle coater 350. Maintaining particles in a dispersed state from manufacture through coating avoids problems associated with agglomeration and redispersion of particles if particles must be redispersed in the liquid feed 102 for feed to the aerosol generator 106. For example, for

particles originally precipitated from a liquid medium, the liquid medium containing the suspended precipitated particles could be used to form the liquid feed 102 to the aerosol generator 106. It should be noted that the particle coater 350 could be an integral extension of the furnace 110 or could be a separate piece of equipment.

In a further embodiment of the present invention, following preparation of the particles 112 in the furnace 110, the particles 112 may then be structurally modified to impart desired physical properties prior to particle collection. Referring now to Fig. 42, one embodiment of the process of the present invention is shown including such structural particle modification. The particles 112 exiting the furnace 110 go to a particle modifier 360 where the particles are structurally modified to form modified particles 362, which are then sent to the particle collector 114 for preparation of the particulate product 116.. The particle modifier 360 is typically a furnace, such as an annealing furnace, which may be integral with the furnace 110 or may be a separate heating device. Regardless, it is important that the particle modifier 360 have temperature control that is independent of the furnace 110, so that the proper conditions for particle modification may be provided separate from conditions required of the furnace 110 to prepare the particles 112. The particle modifier 360, therefore, typically provides a temperature controlled environment and necessary residence time to effect the desired structural modification of the particles 112.

The structural modification that occurs in the particle modifier 360 may be any modification to the crystalline structure or morphology of the particles 112. For example, the particles 112 may be annealed in the particle modifier 360 to densify the particles 112 or to recrystallize the particles 112 into a polycrystalline or single crystalline form. Also, especially in the case of composite particles 112, the particles may be annealed for a sufficient time to permit redistribution within the particles 112 of different material phases. Particularly preferred parameters for such processes are discussed in more detail below.

The initial morphology of composite particles made in the furnace 110, according to the present invention, could take a variety of forms, depending upon the specified materials involved and the specific processing conditions. Examples of some possible composite particle morphologies, manufacturable according to the present invention are shown in Fig. 43. These morphologies could be of the particles as initially produced in

the furnace 110 or that result from structural modification in the particle modifier 360. Furthermore, the composite particles could include a mixture of the morphological attributes shown in Fig. 43.

Referring now to Fig. 44, an embodiment of the apparatus of the present invention is shown that includes the aerosol generator 106 (in the form of the 400 transducer array design), the aerosol concentrator 236 (in the form of a virtual impactor), the droplet classifier 280 (in the form of an impactor), the furnace 110, the particle cooler 320 (in the form of a gas quench cooler) and the particle collector 114 (in the form of a bag filter). All process equipment components are connected via appropriate flow conduits that are substantially free of sharp edges that could detrimentally cause liquid accumulations in the apparatus. Also, it should be noted that flex connectors 370 are used upstream and downstream of the aerosol concentrator 236 and the droplet classifier 280. By using the flex connectors 370, it is possible to vary the angle of slant of vertically extending slits in the aerosol concentrator 236 and/or the droplet classifier 280. In this way, a desired slant for the vertically extending slits may be set to optimize the draining characteristics off the vertically extending slits.

Aerosol generation with the process of the present invention has thus far been described with respect to the ultrasonic aerosol generator. Use of the ultrasonic generator is preferred for the process of the present invention because of the extremely high quality and dense aerosol generated. In some instances, however, the aerosol generation for the process of the present invention may have a different design depending upon the specific application. For example, when larger particles are desired, such as those having a weight average size of larger than about 3 μm, a spray nozzle atomizer may be preferred. For smaller-particle applications, however, and particularly for those applications to produce particles smaller than about 3 μm, and preferably smaller than about 2 μm in size, as is generally desired with the particles of the present invention, the ultrasonic generator, as described herein, is particularly preferred. In that regard, the ultrasonic generator of the present invention is particularly preferred for when making particles with a weight average size of from about 0.2 μm to about 3 μm.

Although ultrasonic aerosol generators have been used for medical applications and home humidifiers, use of ultrasonic generators for spray pyrolysis particle manufacture has largely been confined to small-scale, experimental situations. The

ultrasonic aerosol generator of the present invention described with reference to Figs. 2-21, however, is well suited for commercial production of high quality powders with a small average size and a narrow size distribution. In that regard, the aerosol generator produces a high quality aerosol, with heavy droplet loading and at a high rate of production. Such a combination of small droplet size, narrow size distribution, heavy droplet loading, and high production rate provide significant advantages over existing aerosol generators that usually suffer from at least one of inadequately narrow size distribution, undesirably low droplet loading, or unacceptably low production rate.

Through the careful and controlled design of the ultrasonic generator of the present invention, an aerosol may be produced typically having greater than about 70 weight percent (and preferably greater than about 80 weight percent) of droplets in the size range of from about 1 μm to about 10 μm, preferably in a size range of from about 1 μm to about 5 μm and more preferably from about 2 μm to about 4 μm. Also, the ultrasonic generator of the present invention is capable of delivering high output rates of liquid feed in the aerosol. The rate of liquid feed, at the high liquid loadings previously described, is preferably greater than about 25 milliliters per hour per transducer, more preferably greater than about 37.5 milliliters per hour per transducer, even more preferably greater than about 50 milliliters per hour per transducer and most preferably greater than about 100 millimeters per hour per transducer. This high level of performance is desirable for commercial operations and is accomplished with the present invention with a relatively simple design including a single precursor bath over an array of ultrasonic transducers. The ultrasonic generator is made for high aerosol production rates at a high droplet loading, and with a narrow size distribution of droplets. The generator preferably produces an aerosol at a rate of greater than about 0.5 liter per hour of droplets, more preferably greater than about 2 liters per hour of droplets, still more preferably greater than about 5 liters per hour of droplets, even more preferably greater than about 10 liters per hour of droplets and most preferably greater than about 40 liters per hour of droplets. For example, when the aerosol generator has a 400 transducer design, as described with reference to Figs. 4-21, the aerosol generator is capable of producing a high quality aerosol having high droplet loading as previously described, at a total production rate of preferably greater than about 10 liters per hour of liquid feed, more preferably greater than about 15 liters per hour of liquid feed, even more preferably

greater than about 20 liters per hour of liquid feed and most preferably greater than about 40 liters per hour of liquid feed.

Under most operating conditions, when using such an aerosol generator, total particulate product produced is preferably greater than about 0.5 gram per hour per transducer, more preferably greater than about 0.75 gram per hour per transducer, even more preferably greater than about 1.0 gram per hour per transducer and most preferably greater than about 2.0 grams per hour per transducer.

For the production of oxygen-containing phosphors according to the present invention, the liquid feed includes the chemical components that will form the phosphor particles. For example, the liquid feed can include a solution containing nitrates, chlorides, sulfates, hydroxides or oxalates of the phosphor compound. A preferred precursor are the nitrates, such as yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$, for the production of yttria phosphor particles. Nitrates are typically highly soluble in water and the solutions maintain a low viscosity, even at high concentrations. A typical reaction mechanism would be:

$$2Y(NO_3)_3 + H_2O + \text{heat} \text{ --------> } Y_2O_3 + NO_x + H_2O$$

The solution is preferably not saturated with the precursor to avoid precipitate formation in the liquid. The solution preferably includes, for example, sufficient precursor to yield from about 1 to 50 weight percent, such as from about 1 to 15 weight percent, of the phosphor compound, based on the amount of metals in solution. The final particle size of the phosphor particles is also influenced by the precursor concentration. Generally, lower precursor concentrations in the liquid feed will produce particles having a smaller average size.

In addition to the host material, the liquid feed preferably includes the precursor to the activator ion. For example, for the production of Y_2O_3:Eu phosphor particles, the precursor solution preferably includes yttrium nitrate, as is discussed above, and also europium nitrate. The relative concentrations of the precursors can be adjusted to vary the concentration of the activator ion in the host material.

Preferably, the solvent is aqueous-based for ease of operation, although other solvents, such as toluene, may be desirable. The use of organic solvents can lead to undesirable carbon contamination in the phosphor particles. The pH of the aqueous-

based solutions can be adjusted to alter the solubility characteristics of the precursor in the solution.

In addition to the foregoing, the liquid feed may also include other additives that contribute to the formation of the particles. For example, a fluxing agent can be added to the solution to increase the crystallinity and/or density of the particles. For example, the addition of urea to metal salt solutions, such as a metal nitrate, can increase the density of particles produced from the solution. In one embodiment, up to about 1 mole equivalent urea is added to the precursor solution, as measured against the moles of phosphor compound in the metal salt solution. Further, if the particles are to be coated phosphor particles, as is discussed in more detail below, a soluble precursor to both the oxygen-containing phosphor compound and the coating can be used in the precursor solution wherein the coating precursor is an involatile or volatile species.

For producing oxygen-containing phosphor particles, the carrier gas may comprise any gaseous medium in which droplets produced from the liquid feed may be dispersed in aerosol form. Also, the carrier gas may be inert, in that the carrier gas does not participate in formation of the phosphor particles. Alternatively, the carrier gas may have one or more active component(s) that contribute to formation of the phosphor particles. In that regard, the carrier gas may include one or more reactive components that react in the furnace to contribute to formation of the phosphor particles. In many applications for the production of oxygen-containing phosphor particles, air will be a satisfactory carrier gas. In other instances, a relatively inert gas such as nitrogen may be required.

When the oxygen-containing phosphors are coated phosphors, precursors to metal oxide coatings can be selected from volatile metal acetates, chlorides, alkoxides or halides. Such precursors are known to react at high temperatures to form the corresponding metal oxides and eliminate supporting ligands or ions. For example, $SiCl_4$ can be used as a precursor to SiO_2 coatings when water vapor is present:

$$SiCl_{4\,(g)} + 2H_2O_{(g)} \text{ -------> } SiO_{2(s)} + 4\,HCl_{(g)}$$

$SiCl_4$ also is highly volatile and is a liquid at room temperature, which makes transport into the reactor more controllable.

Metal alkoxides can be used to produce metal oxide films by hydrolysis. The water molecules react with the alkoxide M-O bond resulting in clean elimination of the corresponding alcohol with the formation of M-O-M bonds:

$$Si(OEt)_4 + 2H_2O \text{ --------> } SiO_2 + 4EtOH$$

Most metal alkoxides have a reasonably high vapor pressure and are therefore well suited as coating precursors.

Metal acetates are also useful as coating precursors since they readily decompose upon thermal activation by acetic anhydride elimination:

$$Mg(O_2CCH_3)_2 \text{ ----------> } MgO + CH_3C(O)OC(O)CH_3$$

Metal acetates are advantageous as coating precursors since they are water stable and are reasonably inexpensive.

Coatings can be generated on the particle surface by a number of different mechanisms. One or more precursors can vaporize and fuse to the hot phosphor particle surface and thermally react resulting in the formation of a thin-film coating by chemical vapor deposition (CVD). Preferred coatings deposited by CVD include metal oxides and elemental metals. Further, the coating can be formed by physical vapor deposition (PVD) wherein a coating material physically deposits an the surface of the particles. Preferred coatings deposited by PVD include organic materials and elemental metal. Alternatively, the gaseous precursor can react in the gas phase forming small particles, for example less than about 5 nanometers in size, which then diffuse to the larger particle surface and sinter onto the surface, thus forming a coating. This method is referred to as gas-to-particle conversion (GPC). Whether such coating reactions occur by CVD, PVD or GPC is dependent on the reactor conditions such as precursor partial pressure, water partial pressure and the concentration of particles in the gas stream. Another possible surface coating method is surface conversion of the surface of the particle by reaction with a vapor phase reactant to convert the surface of the particles to a different material than that originally contained in the particles.

In addition, a volatile coating material such as PbO, MoO_3 or V_2O_5 can be introduced into the reactor such that the coating deposits on the particle by condensation. Highly volatile metals, such as silver, can also be deposited by condensation. Further, the phosphor powders can be coated using other techniques. For example, a soluble precursor to both the phosphor powder and the coating can be used in the precursor solution wherein the coating precursor is involatile (e.g. $Al(NO_3)_3$) or volatile (e.g. $Sn(OAc)_4$ where Ac is acetate). In another method, a colloidal precursor and a soluble phosphor precursor can be used to form a particulate colloidal coating on the phosphor.

The structural modification that occurs in the particle modifier may be any modification to the crystalline structure or morphology of the particles. For example, the particles can be annealed in the particle modifier to densify the particles or to recrystallize the particles into a polycrystalline or single crystalline form. Also, especially in the case of composite particles, the particles may be annealed for a sufficient time to permit redistribution within the particles of different material phases or permit redistribution of the activator ion(s).

More specifically, while the oxygen-containing phosphor powders produced by the foregoing method have good crystallinity, it may be desirable to increase the crystallinity (average crystallite size) after production. Thus, the powders can be annealed (heated) for an amount of time and in a preselected environments to increase the crystallinity of the phosphor particles. Increased crystallinity can advantageously yield an increased brightness and efficiency of the phosphor particles. If such annealing steps are performed, the annealing temperature and time should be selected to minimize the amount of interparticle sintering that is often associated with annealing. According to one embodiment of the present invention, the oxygen-containing phosphor powder is preferably annealed at a temperature of from about 700°C to about 1700°C, more preferably from about 1100°C to about 1400°C. The annealing time is preferably not more than about 2 hours and can be as little as about 1 minute. The oxygen-containing powders are typically annealed in an inert gas, such as argon or in an oxygen-containing gas such air.

Further, the crystallinity of the phosphors can be increased by using a fluxing agent, either in the precursor solution or in a post-formation annealing step. A fluxing agent is a reagent which improves the crystallinity of the material when the reagent and the material are heated together, as compared to heating the material to the same temperature and for the same amount of time in the absence of the fluxing agent. The fluxing agents typically cause a eutectic to form which leads to a liquid phase at the grain boundaries, increasing the diffusion coefficient. The fluxing agent, for example alkali metal halides such as NaCl or KCl or an organic compound such as urea ($CO(NH_2)_2$), can be added to the precursor solution where it improves the crystallinity and/or density of the particles during their subsequent formation. Alternatively, the fluxing agent can be contacted with the phosphor powder batches after they have been collected. Upon

annealing, the fluxing agent improves the crystallinity of the phosphor powder, and therefore improves other properties such as the brightness of the phosphor powder. Also, in the case of composite particles 112, the particles may be annealed for a sufficient time to permit redistribution within the particles 112 of different material phases.

The present invention is particularly applicable to oxygen-containing phosphors. Phosphors are materials which are capable of emitting radiation in the visible or ultraviolet spectral range upon excitation, such as excitation by an external electric field or other external energy source. Oxygen-containing phosphors are those phosphors that have a host material that includes oxygen, such as a host material based on a metal oxide, a silicate, borate or aluminate. Examples of such oxygen-containing phosphors are given in more detail below. The oxygen-containing phosphors can be chemically tailored to emit specific wavelengths of visible light, such as red, blue or green light. By dispersing various phosphor powders in a predetermined arrangement and controllably exciting the powders, a full-color visual display can be achieved.

Oxygen-containing phosphors typically include a matrix compound, referred to as a host material, and the phosphor further includes one or more dopants, referred to as activator ions, to emit a specific color or to enhance the luminescence characteristics. Some phosphors, such as up-convertor phosphors, incorporate more than one activator ion.

Phosphors can be classified by their phosphorescent properties and the present invention is applicable to all types of these phosphors. For example, electroluminescent phosphors are phosphors that emit light upon stimulation by an electric field. These phosphors are used for thin-film and thick-film electroluminescent displays, back lighting for LCD's and electroluminescent lamps used in wrist watches and the like. Cathodoluminescent phosphors emit light upon stimulation by electron bombardment. These phosphors are utilized in CRT's (e.g. common televisions) and FED's.

Photoluminescent phosphors emit light upon stimulation by other light. The stimulating light usually has higher energy than the emitted light. For example, a photoluminescent phosphor can emit visible light when stimulated by ultraviolet light. These phosphors are utilized in plasma display panels and common fluorescent lamps.

Up-converter phosphors also emit light upon stimulation by other light, but usually light of a lower energy than the emitted light. For example, infrared light can be

used to stimulate an up-converter phosphor which then emits visible or ultraviolet light. Up-convertor phosphors typically include at least 2 activator ions which convert the lower energy infrared light. These materials are useful in immunoassay and security applications. Similarly, x-ray phosphors are utilized to convert x-rays to visible light and are useful in medical diagnostics.

The oxygen-containing host material can be doped with an activator ion, such as in an amount of from about 0.02 to about 15 atomic percent, preferably from about 0.02 to about 10 atomic percent and more preferably from about 0.02 to about 5 atomic percent. It will be appreciated, as is discussed in more detail below, that the preferred concentration of activator ion in the host material can vary for different applications. In the case of the phosphor compound ZnO, the metal oxide is produced to be slightly off-stoichiometric such that Zn is the activator ion.

One advantage of the present invention is that the activator ion is homogeneously distributed throughout the host material. Phosphor powders prepared by solid-state methods do not give uniform concentration of the activator ion in small particles and solution routes also do not give homogenous distribution of the activator ion due to different rates of precipitation.

Particular phosphor compounds may be preferred for certain applications and no single phosphor compound is necessarily preferred for all possible applications. As used herein, oxygen-containing phosphor compounds are those that include a host material selected from simple or complex metal oxides, metal silicates, metal borates, or titanates.

Examples of metal oxide phosphor compounds include, but are not limited to, Y_2O_3:Eu, ZnO:Zn, $Y_3Al_5O_{12}$:Tb and barium aluminates, such as $BaMgAl_{14}O_{23}$:Eu.

Examples of metal silicate phosphors include silicates such as Zn_2SiO_4:Mn, Ca_2SiO_4:Eu, Ba_2SiO_4:Eu, Gd_2SiO_5:Ce and Y_2SiO_5:Ce. Examples of metal borates include (Y,Gd)BO_3:Eu. An example of a titanate is $CaTiO_3$:RE, where RE is a rare-earth element.

Particularly preferred oxygen-containing phosphor host materials for some display applications include ZnO:Zn and Y_2O_3:Eu. Further examples of preferred oxygen-containing phosphor host materials and activator ions are listed in Table I.

TABLE I Examples of Oxygen-containing Phosphor Materials

Host Material	Activator Ion	Color
ZnO	Zn	Green
Y_2O_3	Eu	Red
$BaMgAl_{14}O_{23}$	Eu	Blue
$Y_3Al_5O_{12}$	Tb	Green
Zn_2SiO_4	Mn	Green
Ca_2SiO_4	Eu	Green
Ba_2SiO_4	Eu	Green
Y_2SiO_5	Ce	Blue
(Y,Gd) BO_3	Eu	Red

According to the present invention, the oxygen-containing phosphor powder includes particles having a small average size. Although the preferred average size of the phosphor particles will vary according to the application of the phosphor powder, the average particle size of the phosphor particles is not greater than about 10 μm. For most applications, the average particle size is preferably not greater than about 5 μm, such as from about 0.1 μm to about 5 μm and more preferably is not greater than about 3 μm, such as from about 0.3 μm to about 3 μm. As used herein, the average particle size is the weight average particle size.

According to the present invention, the powder batch of phosphor particles also has a narrow particle size distribution, such that the majority of particles are substantially the same size. Preferably, at least about 90 weight percent of the particles and more preferably at least about 95 weight percent of the particles are not larger than twice the average particle size. Thus, when the average particle size is about 2 μm, it is preferred that at least about 90 weight percent of the particles are not larger than 4μm and it is more preferred that at least about 95 weight percent of the particles are not larger than 4μm. Further, it is preferred that at least about 90 weight percent of the particles, and more preferably at least about 95 weight percent of the particles, are not larger than about 1.5 times the average particle size. Thus, when the average particle size is about 2 μm, it is preferred that at least about 90 weight percent of the particles are not larger than about

3μm and it is more preferred that at least about 95 weight percent of the particles are not larger than about 3 μm.

The phosphor particles of the present invention can be substantially single crystal particles or may be comprised of a number of crystallites. According to the present invention, the phosphor particles are highly crystalline and it is preferred that the average crystallite size approaches the average particle size such that the particles are mostly single crystals or are composed of only a few large crystals. The average crystallite size of the particles is preferably at least about 25 nanometers, more preferably is at least about 40 nanometers, even more preferably is at least about 60 nanometers and most preferably is at least about 80 nanometers. In one embodiment, the average crystallite size is at least about 100 nanometers. As it relates to particle size, the average crystallite size is preferably at least about 20 percent, more preferably at least about 30 percent and most preferably is at least about 40 percent of the average particle size. Such highly crystalline phosphors are believed to have increased luminescent efficiency and brightness as compared to phosphor particles having smaller crystallites.

The oxygen-containing phosphor particles of the present invention advantageously have a high degree of purity, that is, a low level of impurities. Impurities are those materials that are not intended in the final product. Thus, an activator ion is not considered an impurity. The level of impurities in the phosphor powders of the present invention is preferably not greater than about 1 atomic percent, more preferably is not greater than about 0.1 atomic percent and even more preferably is not greater than about 0.01 atomic percent.

The oxygen-containing phosphor particles are also very dense (not porous) as measured by helium pychnometry. Preferably, the particles have a particle density of at least about 80 percent of the theoretical density for the host material, more preferably at least about 90 percent of the theoretical density for the host material and even more preferably at least about 95 percent of the theoretical density for the host material.

The oxygen-containing phosphor particles of the present invention are also substantially spherical in shape. That is, the particles are not jagged or irregular in shape. Spherical particles are particularly advantageous because they are able to disperse and coat a device, such as a display panel, more uniformly with a reduced average thickness.

Although the particles are substantially spherical, the particles may become faceted as the crystallite size increases and approaches the average particle size.

In addition, the oxygen-containing phosphor particles according to the present invention advantageously have a low surface area. The particles are substantially spherical, which reduces the total surface area for a given mass of powder. Further, the elimination of larger particles from the powder batches eliminates the porosity that is associated with open pores on the surface of such larger particles. Due to the elimination of the large particles, the powder advantageously has a lower surface area. Surface area is typically measured using a BET nitrogen adsorption method which is indicative of the surface area of the powder, including the surface area of accessible surface pores on the surface of the powder. For a given particle size distribution, a lower value of a surface area per unit mass of powder indicates solid or non-porous particles. Decreased surface area reduces the susceptibility of the phosphor powders to adverse surface reactions, such as degradation from moisture. This characteristic can advantageously extend the useful life of the phosphor powders.

The surfaces of the oxygen-containing phosphor particles according to the present invention are typically smooth and clean with a minimal deposition of contaminants on the particle surface. For example, the outer surfaces are not contaminated with surfactants, as is often the case with particles produced by liquid precipitation routes.

In addition, the powder batches of oxygen-containing phosphor particles according to the present invention are substantially unagglomerated, that is, they include substantially no hard agglomerates or particles. Hard agglomerates are physically coalesced lumps of two or more particles that behave as one large particle. Agglomerates are disadvantageous in most applications of phosphor powders. It is preferred that no more than about 1 weight percent of the phosphor particles in the powder batch of the present invention are in the form of hard agglomerates. More preferably, no more than about 0.5 weight percent of the particles are in the form of hard agglomerates and even more preferably no more than about 0.1 weight percent of the particles are in the form of hard agglomerates.

According to one embodiment of the present invention, the oxygen-containing phosphor particles are composite phosphor particles, wherein the individual particles include at least one oxygen-containing phosphor phase and at least a second phase

associated with the phosphor phase. The second phase can be a different phosphor compound or can be a non-phosphor compound. Such composites can advantageously permit the use of phosphor compounds in devices that would otherwise be unusable. Further, combinations of different phosphor compounds within one particle can produce emission of a selected color. The emission of the two phosphor compounds would combine to approximate white light. Further, in cathodoluminescent applications, the matrix material can accelerate the impingent electrons to enhance the luminescence.

According to another embodiment of the present invention, the phosphor particles are surface modified or coated phosphor particles that include a particulate coating (Fig. 43d) for non-particulate (film) coating (Fig. 43a) that substantially encapsulates an outer surface of the particles. The coating can be a metal, a non-metallic compound or an organic compound.

Coatings are often desirable to reduce degradation of the oxygen-containing phosphor material due to moisture or other influences, such as the plasma in a plasma display device or high density electron bombardment in cathodoluminescent devices. The thin, uniform coatings according to the present invention will advantageously permit use of the phosphor powders under low voltage, high current conditions. Coatings also create a diffusion barrier such that activator ions (e.g. Cu and Mn) cannot transfer from one particle to another, thereby altering the luminescence characteristics. Coatings can also control the surface energy levels of the particles.

The coating can be a metal, metal oxide or other inorganic compound such as a metal sulfide, or can be an organic compound. For example, a metal oxide coating can advantageously be used, such as a metal oxide selected from the group consisting of SiO_2, MgO, Al_2O_3, ZnO, SnO_2 or In_2O_3. Particularly preferred are SiO_2 and Al_2O_3 coatings. Semiconductive oxide coatings such as SnO_2 or In_2O_3 can be advantageous in some applications due to the ability of the coating to absorb secondary electrons that are emitted by the phosphor. Metal coatings, such as copper, can be useful for phosphor particles used in direct current electroluminescent applications. In addition, phosphate coatings, such as zirconium phosphate or aluminum phosphate, can also be advantageous for use in some applications.

The coatings should be relatively thin and uniform. The coating should encapsulate the entire particle, but be sufficiently thin such that the coating doesn't

interfere with light transmission. Preferably, the coating has an average thickness of not greater than about 200 nanometers, more preferably not greater than about 100 nanometers, and even more preferably not greater than about 50 nanometers. The coating preferably completely encapsulates the phosphor particle and therefore should have an average thickness of at least about 2 nanometers, more preferably at least about 5 nanometers. In one embodiment, the coating has a thickness of from about 2 to 50 nanometers, such as from about 2 to 10 nanometers. Further, the particles can include more than one coating substantially encapsulating the particles to achieve the desired properties.

The coating, either particulate or non-particulate, can also include a pigment or other material that alters the light characteristics of the phosphor. Red pigments can include compounds such as the iron oxides (Fe_2O_3), cadmium sulfide compounds (CdS) or mercury sulfide compounds (HgS). Green or blue pigments include cobalt oxide (CoO), cobalt aluminate ($CoAl_2O_4$) or zinc oxide (ZnO). Pigment coatings are capable of absorbing selected wavelengths of light leaving the phosphor, thereby acting as a filter to improve the color contrast and purity, particularly in CRT devices.

In addition, the phosphor particles can be coated with an organic compound such as PMMA (polymethylmethacrylate), polystyrene or similar organic compounds, including surfactants that aid in the dispersion and/or suspension of the particles in a flowable medium. The organic coating is preferably not greater than about 100 nanometers thick and is substantially dense and continuous about particle. The organic coatings can advantageously prevent corrosion of the phosphor particles, especially in electroluminescent lamps, and also can improve the dispersion characteristics of the particles in a paste or other flowable medium.

The coating can also be comprised of one or more monolayer coatings, such as from about 1 to 3 monolayer coatings. A monolayer coating is formed by the reaction of an organic or an inorganic molecule with the surface of the phosphor particles to form a coating layer that is essentially one molecular layer thick. In particular, the formation of a monolayer coating by reaction of the surface of the phosphor powder with a functionalized organo silane such as halo- or amino-silanes, for example hexamethyldisilazane or trimethylsilylchloride, can be used to modify and control the hydrophobicity and hydrophilicity of the phosphor powders. Monolayer coatings of

metal oxides (e.g. ZnO or SiO_2) or metal sulfides (e.g. Cu_2S) can be formed as monolayer coatings. Monolayer coatings can allow for greater control over the dispersion characteristics of the phosphor powder in a wide variety of paste compositions and other flowable mediums.

The monolayer coatings may also be applied to phosphor powders that have already been coated with an organic or inorganic coating, thus providing better control over the corrosion characteristics (through the use of a thicker coating) as well as dispersibility (through the use of a monolayer coating) of the phosphor powder.

As a direct result of the foregoing powder characteristics, the oxygen-containing phosphor powders of the present invention have many unique and advantageous properties that are not found in phosphor powders known heretofore.

The oxygen-containing phosphor powders of the present invention have a high efficiency, sometimes referred to as quantum efficiency. Efficiency is the overall conversion rate of excitation energy (electrons or photons) to visible photons emitted. According to one embodiment of the present invention, the efficiency of the phosphor powder is at least about 90%. The near perfect efficiency of the phosphor powders according to the present invention is believed to be due to the high crystallinity and homogenous distribution of activator ion in the host material.

The oxygen-containing phosphor powders also have well-controlled color characteristics, sometimes referred to as emission spectrum characteristics or chromaticity. This important property is due to the ability to precisely control the composition of the host material, the homogenous distribution of the activator ion and the high purity of the powders.

The phosphor powders also have improved decay time, also referred to as persistence. Persistence is referred to as the amount of time for the light emission to decay to 10% of its brightness. Phosphors with long decay times can result in blurred images when the image moves across the display. The improved decay time of the phosphor powders of the present invention is believed to be due primarily to the homogenous distribution of activator ion in the host material.

The phosphor powders also have an improved brightness over prior art phosphor powders. That is, under a given application of energy, the phosphor powders of the present invention produce more light.

Thus, the oxygen-containing phosphor powders of the present invention have a unique combination of properties that are not found in conventional phosphor powders . The powders can advantageously be used to form a number of intermediate products, for example pastes or slurries, and can be incorporated into a number of devices, wherein the devices will have significantly improved performance resulting directly from the characteristics of the phosphor powders of the present invention. The devices can include light-emitting lamps and display devices for visually conveying information and graphics. Such display devices include traditional CRT-based display devices, such as televisions, and also include flat panel displays. Flat panel displays are relatively thin devices that present graphics and images without the use of a traditional picture tube and operate with modest power requirements. Generally, flat panel displays include a phosphor powder selectively dispersed on a viewing panel, wherein the excitation source lies behind and in close proximity to the panel. Flat panel displays include liquid crystal displays (LCD), plasma display panels (PDP's) electroluminescent (EL) displays, and field emission displays (FED'S).

CRT devices, utilizing a cathode ray tube, include traditional display devices such as televisions and computer monitors. CRT's operate by selectively firing electrons from one or more cathode ray tubes at cathodoluminescent phosphor particles which are located in predetermined regions (pixels) of a display screen. The cathode ray tube is located at a distance from the display screen which increases as screen size increases. By selectively directing the electron beam at certain pixels, a full color display with high resolution can be achieved.

Flat panel displays (FPD's) offer many advantages over CRT's including lighter weight, portability and decreased power requirements. Flat panel displays can be either monochrome or color displays. It is believed that flat panel displays will eventually replace the bulky CRT devices, such as televisions, with a thin product that can be hung on a wall, like a picture. Currently, flat panel displays can be made thinner, lighter and with lower power consumption than CRT devices, but not with the visual quality and cost performance of a CRT device.

The high electron voltages and small currents traditionally required to activate phosphors efficiently in a CRT device have hindered the development of flat panel displays. Phosphors for flat panel displays such as field emission displays must typically

operate at a lower voltage, higher current density and higher efficiency than phosphors used in existing CRT devices. The low voltages used in such displays result in an electron penetration depth in the range of several micrometers down to tens of nanometers, depending on the applied voltage. Thus, the control of the size and crystallinity of the phosphor particles is critical to device performance. If large or agglomerated powders are used, only a small fraction of the electrons will interact with the phosphor. Use of phosphor powders having a wide size distribution can also lead to non-uniform pixels and sub-pixels, which will produce a blurred image.

One type of FPD is a plasma display panel (PDP). Plasma displays have image quality that is comparable to current CRT devices and can be easily scaled to large sizes such as 20 to 60 diagonal inches. The displays are bright and lightweight and have a thickness of from about 1.5 to 3 inches. A plasma display functions in a similar manner as fluorescent lighting. In a plasma display, plasma source, typically a gas mixture, is placed between an opposed array of addressable electrodes and a high energy electric field is generated between the electrodes. Upon reaching a critical voltage, a plasma is formed from the gas and UV photons are emitted by the plasma. Color plasma displays contain three-color photoluminescent phosphor particles deposited on the inside of the glass faceplate. The phosphors selectively emit light when illuminated by the photons. Plasma displays operate at relatively low currents and can be driven either by an AC or DC signal. AC plasma systems use a dielectric layer over the electrode, which forms a capacitor. This impedance limits current and provides a necessary charge in the gas mixture.

Oxygen-containing phosphors according to the present invention which are particularly useful for plasma displays include $(Y,Gd)BO_3$:Eu for red, $Y_3Al_5O_{12}$:Tb for blue/green, Zn_2SiO_4:Mn for green and $BaMgAl_{14}O_{23}$:Eu for blue. The phosphors can advantageously be coated, such as with MgO, to reduce degradation from the plasma.

Another type of flat panel display is a field emission display (FED). These devices advantageously eliminate the size, weight and power consumption problems of CRT's while maintaining comparable image quality, and therefore are particularly useful for portable electronics, such as for laptop computers. FED's generate electrons from millions of cold microtip emitters with low power emission that are arranged in a matrix addressed array with several thousand emitters allocated to each pixel in the display. The

microtip emitters are located approximately 0.2 millimeter from a cathodoluminescent phosphor screen which generates the display image. This allows for a thin, light-weight display.

Oxygen-containing phosphors which are particularly useful for FED devices include Y_2O_3:Eu for red, ZnO for green and BAM:Eu for blue. These phosphors can be coated, such as with a metal oxide, since the high electron beam current densities can cause breakdown and dissociation of the phosphor host material. Dielectric coatings such as SiO_2 and Al_2O_3 can be used. Further, semiconducting coatings such as SnO_2 or In_2O_3 can be particularly advantageous to absorb secondary electrons.

Coatings for the oxygen-containing FED phosphors preferably have an average thickness of from about 1 to 10 nanometers, more preferably from about 1 to 5 nanometers. Coatings having a thickness in excess of about 10 nanometers will decrease the brightness of the device since the electron penetration depth of 1-2 kV electrons is only about 10 nanometers. Such thin coatings can advantageously be monolayer coatings, as is discussed above.

The primary obstacle to further development of FED's is the lack of adequate phosphor powders. FED's require low-voltage phosphor materials, that is, phosphors which emit sufficient light under low applied voltages, such as less than about 500 volts, and high current densities. The oxygen-containing phosphor powders of the present invention advantageously have improved brightness under such low applied voltages and the coated phosphor particles resist degradation under high current densities. The improved brightness can be attributed to the high crystallinity and high purity of the particles. Phosphor particles with low crystallinity and high impurities due to processes such as milling do not have the desirable high brightness. The phosphor particles of the present invention also have the ability to maintain the brightness and chromaticity over long periods of time, such as in excess of 10,000 hours. Further, the spherical morphology of the phosphor powder improves light scattering and therefore improves the visual properties of the display. The small average size of the particles is advantageous since the electron penetration depth is only several nanometers, due to the low applied voltage.

For each of the foregoing display devices, cathode ray tube devices and flat panel display devices including plasma display panels and field emission devices, it is

important for the phosphor layer constituting a pixel to be as thin and uniform as possible with a minimal number of voids. In a preferred embodiment, the phosphor layer constituting the pixel has an average thickness of not greater than about 3 times the average particle size of the powder, preferably not greater than about 2 times the average particle size and even more preferably not greater than about 1.5 times the average particle size. This unique characteristic is possible due to the unique combination of small particle size, narrow size distribution and spherical morphology of the phosphor particles. The device will therefore produce an image having much higher resolution due to the ability to form smaller, more uniform pixels and much higher brightness since light scattering is significantly reduced and the amount of light lost due to non-luminescent particles is reduced.

Electroluminescent displays (EL displays) work by electroluminescence. EL displays are very thin structures which can have very small screen sizes, such as few inches diagonally, while producing a very high resolution image. These displays, due to the very small size, are utilized in many military applications where size is a strict requirement such as in aircraft cockpits, small hand-held displays and heads-up displays. These displays function by applying a high electric potential between two addressing electrodes. EL displays are most commonly driven by an A.C. electrical signal. The electrodes are in contact with a semiconducting phosphor thin-film and the large potential difference creates hot electrons which move through the phosphor, allowing for excitation followed by light emission.

While current electroluminescent display configurations utilize a thin film phosphor layer 1122 and do not typically utilize phosphor powders, the use of very small monodispersed phosphor particles according to the present invention is advantageous for use in such devices. For example, small monodispersed particles could be deposited on a glass substrate using a thick film paste and sintered to produce a well connected film and therefore could replace the expensive and material-limited CVD technology currently used to deposit such films. Such a well-connected film could not be formed from large, agglomerated phosphor particles. Similarly, composite phosphor particles are a viable alternative to the relatively expensive multilayer stack currently employed in electroluminescent displays. Thus, a composite phosphor particle comprising the phosphor and a dielectric material could be used.

Another use for phosphor powders according to the present invention is in the area of electroluminescent lamps. Electroluminescent lamps are formed on a rigid or flexible substrate, such as a polymer substrate, and are commonly used as back lights for membrane switches, cellular phones, watches, personal digital assistants and the like. Additional colors, higher reliability and higher brightness powders are critical needs for the electroluminescent lamp industry to supply designers with the ability to penetrate new market segments. The phosphor layers should also be thinner and denser, without sacrificing brightness, to minimize water intrusion and eliminate light scattering. Higher brightness electroluminescent lamps require thinner phosphor layers, which requires smaller particle size phosphor powders that cannot produced by conventional methods. Such thinner layers will also use less phosphor powder. Presently available EL lamps utilize powders having an average size of about 5 μm or higher, typically much higher. The phosphor powders of the present invention having a small particle size and a narrow size distribution will enable the production of brighter and more reliable EL lamps that have an increased life-expectancy. Further, the phosphor powders of the present invention will enable the production of EL lamps wherein the phosphor layer has a significantly reduced thicknes, without sacraficing brightness or other desirable properties. Conventional EL lamps have phosphor layers on the order of 100 μm thick. The powders of the present invention advantageously enable the production of an EL lamp having a phosphor layer that is not greater than about 15 μm thick, such as not greater than about 10 μm thick. The phosphor layer is preferably not thicker than about 3 times the weight average particle size, more preferably not greater than about 2 times the weight average particle size.

As stated above, electroluminescent lamps are becoming increasingly important for back lighting alphanumeric displays in small electronic devices such as cellular phones, pagers, personal digital assistance, wrist watches, calculators and the like. They are also useful in applications such as instrument panels, portable advertising displays, safety lighting, emergency lighting for rescue and safety devices, photographic backlighting, membrane switches and other similar applications. One of the problems associated with electroluminescent devices is that they generally require the application of alternating current (AC) voltage to produce light. A significant obstacle to the development of the useful direct current electroluminescent (DCEL) devices is a need for

a phosphor powder that will function adequately under a DC electric field. The phosphor powder for functioning under a DC electric field should meet at least three requirements: 1) the particles should have a small average particle size; 2) the particles should have a uniform size, that is, the particle should have a narrow size distribution with no large particles or agglomerates; and 3) the particles should have good luminescence properties, particularly a high brightness. The phosphor powders of the present invention advantageously meet these requirements. Therefore, the phosphor powders of the present invention will advantageously permit the use of electroluminescent devices without requiring an inverter to convert a DC voltage to an AC voltage. Such devices are not commercially available at this time. When utilized in a device applying DC voltage, it is preferred to coat the phosphor particles with a thin layer of a conductive metal, such as copper, or a conductive compound such as copper sulfide.

For many of the foregoing applications, phosphor powders are often dispersed within a paste which is then applied to a surface to obtain a phosphorescent layer. These pastes are commonly used for electroluminescent lamps, FED's, plasma displays, CRT's, lamp phosphors and thick-film electroluminescent displays. The powders of the present invention offer many advantages when dispersed in such a paste. For example, the powders will disperse better than non-spherical powders of wide size distribution and can therefore produce thinner and more uniform layers with a reduced lump count. Such a thick film paste will produce a brighter display. The packing density of the phosphors will also be higher. The number of processing steps can also be advantageously reduced. For example, in the preparation of electroluminescent lamps, two dielectric layers are often needed to cover the phosphor paste layer because many of the phosphor particles will be large enough to protrude through one layer. Spherical particles that are substantially uniform in size will eliminate this problem and the EL lamp will advantageously require one dielectric layer.

EXAMPLES

Y_2O_3 Phosphors

To demonstrate the advantages of the present invention, europium doped yttria phosphors (Y_2O_3:Eu^{3+}) were prepared under a variety of conditions. This phosphor compound is a red phosphor with a peak excitation wavelength at 253 nanometers. This

phosphor compound is one of the most widely used red phosphors and is useful in many applications.

For each of these examples, the powders were produced in accordance with the teachings of the present invention. An aerosol of a precursor solution was generated using an ultrasonic atomization technique. The ultrasonic transducers had a frequency of about 1.6 MHz. The droplets were carried through a tubular furnace in a carrier gas (air) without classifying the droplets with an impactor. The average residence time of the particles in the furnace was estimated to be about 10 seconds. The precursors were yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$ and europium nitrate ($Eu(NO_3)_3 \cdot 6H_2O$). Except as noted, the concentration of the precursors for all experiments yielded 2.9 weight percent yttria in the solution, or 10 grams yttrium nitrate per 100 ml of water.

A first set of experiments was conducted to determine the optimum reaction temperature for producing Y_2O_3 :Eu with 1 atomic percent europium. The reaction temperature was varied at 100°C intervals between 700°C and 1500°C. The relative photoluminescent intensity increased from 700°C to 1000°C and peaked at a reaction temperature of 1000°C. From 1000°C to 1500°C, the relative intensity steadily decreased. Also, the average crystallite size of the powders steadily increased with reaction temperature from 700°C to 1500°C, and increased from about 15 nanometers (700°C) to about 50 nanometers (1500°C). The average crystallite size at 1000°C was about 28 nanometers.

Based on the foregoing, further examples were prepared at a reaction temperature of 1000°C. The europium concentration was varied from about 1 atomic percent to about 15 atomic percent. The relative photoluminescent intensity of the powders increased steadily to about 11 atomic percent Eu, and then rapidly decreased. The maximum intensity occurred at an Eu level of about 11 atomic percent. It is believed that phosphor powders produced according to the present invention can advantageously incorporate this increased amount of activator ion due to the improved atomic mixing of the activator ion in the host lattice, permitting higher amounts of activator ion to be utilized during luminescence.

To determine the effect of annealing on the Y_2O_3:Eu powders of the present invention, powders incorporating 2 atomic percent Eu that were produced at 1000°C were annealed under varying conditions to determine the effect of the annealing

temperature. The powder was placed in a quartz boat and heated at a rate of 10°C per minute and allowed to dwell at a maximum temperature for about 6 minutes in stagnant air. The annealing temperature was varied from 1000°C to 1600°C. The highest relative photoluminescent intensity was observed at an annealing temperature of 1500°C. At annealing temperatures below about 1400°C, the brightness of the powder changed little. The average crystallite size increased steadily from about 22 nanometers to about 68 nanometers at 1500°C. It was also observed that when the brightest non-annealed powder (produced at 1000°C with 10 atomic percent Eu) was annealed at 1400°C for about 6 minutes, the photoluminescent intensity increased by about 55%.

In a further set of Examples, urea was added to the precursor solution to increase the density of the Y_2O_3:Eu phosphor. Specifically, urea in amounts ranging from 0.5 mole equivalents to about 4 mole equivalents were added to the precursor solution. The bulk density was measured using a standard helium pychnometry technique. When produced without urea, the particles had a density of about 4.1 g/cc, which is slightly greater than 80 percent of the theoretical density (5.01 g/cc). The addition of 0.5 mole equivalents of urea increased the density to about 5.0 g/cc or 99% of the theoretical density. One mole equivalent of urea yielded a powder having slightly decreased density, about 4.95. Higher additions of urea produced powder having a steadily decreasing density.

Further experiments were conducted to determine the optimum concentration of the nitrate precursor to yield the highest production rate. The solubility of the nitrate salt in a water solution is about 57.3 weight percent which corresponds to about 28 weight percent yttria. Solutions were prepared that incorporated 5, 10 and 20 weight percent Y_2O_3. The highest production rate occurred with the 5 weight percent solution. Higher concentrations of the precursor appeared to produce exploded particles with many fragments and debris. The best morphology was produced at 5 weight percent yttria since the powder had minimal debris.

Using similar process parameters, other oxygen-containing phosphors were produced. For example, a ZnO:Zn intrinsic phosphor powder was produced in a similar fashion from a zinc nitrate precursor at a reactor temperature of from about 700°C to about 900°C. The degree to which the ZnO is reduced, and hence the luminescence characteristics, can advantageously be controlled by varying the carrier gas composition.

A ZnO:Zn phosphor powder produced according to the present invention is illustrated in Fig. 45. The powder has a small average particle size and consists of particles having a substantially spherical morphology.

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.

What is Claimed is:

1. A powder batch comprising oxygen-containing phosphor particles, wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

2. A powder batch as recited in Claim 1, wherein at least about 95 weight percent of said phosphor particles are not larger than twice said average particle size.

3. A powder batch as recited in Claim 1, wherein at least about 90 weight percent of said phosphor particles are not larger than 1.5 times said average particle size.

4. A powder batch as recited in Claim 1, wherein said average particle size is from about 0.3 μm to about 3 μm.

5. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a metal oxide host-material selected from the group consisting of ZnO, Y_2O_3, $Y_3Al_5O_{12}$ and barium aluminates.

6. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a silicate host-material selected from the group consisting of Zn_2SiO_4, Ca_2SiO_4, Ba_2SiO_4, Gd_2SiO_5 and Y_2SiO_5.

7. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a borate host material.

8. A powder batch as recited in Claim 1, wherein said phosphor particles comprise $(Y,Gd)BO_3$.

9. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a titanate host material.

10. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a host material consisting essentially of ZnO.

11. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a host material consisting essentially of Y_2O_3.

12. A powder batch as recited in Claim 1, wherein said phosphor particles comprise at least a first activator ion.

13. A powder batch as recited in Claim 1, wherein said phosphor particles comprise from about 0.02 to about 15 atomic percent of an activator ion.

14. A powder batch as recited in Claim 1, wherein said phosphor particles comprise a Y_2O_3 host material and Eu as an activator ion.

15. A powder batch as recited in Claim 1, wherein said phosphor particles have an average crystallite size of at least about 25 nanometers.

16. A powder batch as recited in Claim 1, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

17. A powder batch as recited in Claim 1, wherein said phosphor particles are substantially spherical.

18. A powder batch as recited in Claim 1, wherein no greater than about 1 weight percent of said phosphor particles are in the form of hard agglomerates.

19. A powder batch as recited in Claim 1, wherein said phosphor particles are coated particles comprising a substantially uniform coating on an outer surface thereof.

20. A powder batch comprising ZnO phosphor particles, wherein said ZnO phosphor particles have a weight average particle size of not greater than about 5μm and a particle size distribution wherein at least about 90 weight percent of said phosphor particles are not larger than twice said average particle size.

21. A powder batch as recited in Claim 20, wherein said phosphor particles further comprise Zn as an activator ion.

22. A powder batch as recited in Claim 20, wherein said phosphor particles comprise crystallites having an average crystallite size of at least about 25 nanometers.

23. A powder batch as recited in Claim 20, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

24. A powder batch as recited in Claim 20 wherein said phosphor particles are substantially spherical.

25. A powder batch as recited in Claim 20, wherein said average particle size is from about 0.3 to about 3 μm.

26. A powder batch comprising Y_2O_3 phosphor particles , wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

27. A powder batch as recited in Claim 26, wherein said phosphor particles further comprise Eu as an activator ion.

28. A powder batch as recited in Claim 26, wherein said phosphor particles have an average crystallite size of at least about 25 nanometers.

29. A powder batch as recited in Claim 26, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

30. A powder batch as recited in Claim 26, wherein said phosphor particles are substantially spherical.

31. A powder batch as recited in Claim 26, wherein said phosphor particles comprise an activator ion homogeneously distributed throughout said particles.

32. A powder batch as recited in Claim 26, wherein said average particle size is from about 0.3 to about 3 μm.

33. A powder batch comprising $Y_3Al_5O_{12}$ phosphor particles, wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

34. A powder batch as recited in Claim 33, wherein said phosphor particles further comprise Tb as an activator ion.

35. A powder batch as recited in Claim 33, wherein said phosphor particles have an average crystallite size of at least about 25 nanometers.

36. A powder batch as recited in Claim 33, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

37. A powder batch as recited in Claim 33, wherein said phosphor particles are substantially spherical.

38. A powder batch as recited in Claim 33, wherein said phosphor particles comprise an activator ion homogeneously distributed throghout said particles.

39. A powder batch as recited in Claim 33, wherein said average particle size is from about 0.3 to about 3 μm.

40. A powder batch comprising barium aluminate phosphor particles, wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

41. A powder batch as recited in Claim 40, wherein said phosphor particles comprise $BaMgAl_{17}O_{23}$.

42. A powder batch as recited in Claim 40, wherein said phosphor particles further comprise Eu as an activator ion.

43. A powder batch as recited in Claim 40, wherein said phosphor particles have an average crystallite size of at least about 25 nanometers.

44. A powder batch as recited in Claim 40, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

45. A powder batch as recited in Claim 40, wherein said phosphor particles are substantially spherical.

46. A powder batch as recited in Claim 40, wherein said phosphor particles comprise an activator ion homogeneously distributed throghout said particles.

47. A powder batch as recited in Claim 40, wherein said average particle size is from about 0.3 to about 3 μm.

48. A powder batch comprising metal silicate phosphor particles, wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

49. A powder batch as recited in Claim 48, wherein said metal silicates are selected from the group consisting of Zn_2SiO_4, Ca_2SiO_4, Ba_2SiO_4, Gd_2SiO_5 and Y_2SiO_5.

50. A powder batch as recited in Claim 48, wherein said phosphor particles further comprise an activator ion selected from the group consisting of rare-earth elements and Mn.

51. A powder batch as recited in Claim 48, wherein said phosphor particles have an average crystallite size of at least about 25 nanometers.

52. A powder batch as recited in Claim 48, wherein said phosphor particles have an average crystallite size of at least about 40 nanometers.

53. A powder batch as recited in Claim 48, wherein said phosphor particles are substantially spherical.

54. A powder batch as recited in Claim 48, wherein said phosphor particles comprise an activator ion homogeneously distributed throghout said particles.

55. A powder batch as recited in Claim 48, wherein said average particle size is from about 0.3 to about 3 μm.

56. A powder batch comprising oxygen-containing phosphor particles, wherein said phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size and wherein said phosphor particles comprise at least a first coating on an outer surface thereof.

57. A powder batch as recited in Claim 56, wherein said average particle size is from about 0.3 μm to about 3 μm.

58. A powder batch as recited in Claim 56, wherein said coating substantially fully encapsulates said phosphor particles.

59. A powder batch as recited in Claim 56, wherein said coating is a substantially uniform non-particulate coating.

60. A powder batch as recited in Claim 56, wherein said coating is a substantially uniform particulate coating.

61. A powder batch as recited in Claim 56, wherein said coating has an average thickness of not greater than about 100 nanometers.

62. A powder batch as recited in Claim 56, wherein said coating has an average thickness of from about 2 nanometers to about 10 nanometers.

63. A powder batch as recited in Claim 56, wherein said phosphor particles further comprise a second coating substantially fully encapsulating said first coating.

64. A powder batch as recited in Claim 56, wherein said phosphor particles comprise crystallites having an average crystallite size of at least about 25 nanometers.

65. A powder batch as recited in Claim 56, wherein said phosphor particles are substantially spherical.

66. A powder batch as recited in Claim 56, wherein said coating consists essentially of a metal.

67. A powder batch as recited in Claim 56, wherein said first coating comprises a pigment.

68. A powder batch as recited in Claim 56, wherein said coating comprises an organic compound.

69. A powder batch as recited in Claim 56, wherein said coating comprises a metal oxide.

70. A powder batch comprising composite oxygen-containing phosphor particles, wherein said composite phosphor particles have a weight average particle size of not greater than about 5 μm and a particle size distribution wherein at least about 90 weight percent of said particles are smaller than twice said average particle size and wherein said phosphor particles comprise at least a first oxygen-containing phosphor compound phase and at least a second phase.

71. A powder batch as recited in Claim 70, wherein said second phase comprises a second oxygen-containing phosphor compound.

72. A powder batch as recited in Claim 70, wherein said second phase comprises a metal sulfide phosphor compound.

73. A powder batch as recited in Claim 70, wherein said particles are substantially spherical.

74. A method for the production of oxygen-containing phosphor particles, comprising the steps of:

a) generating an aerosol of droplets from a liquid wherein said liquid comprises a oxygen-containing phosphor precursor and wherein said droplets have a size distribution such that at least about 80 weight percent of said droplets have a size of from about 1 μm to about 5 μm;

b) moving said droplets in a carrier gas; and

c) heating said droplets to remove liquid therefrom and form oxygen-containing phosphor particles.

75. A method as recited in Claim 74, wherein said carrier gas comprises air.

76. A method as recited in Claim 74, wherein said heating step comprises passing said droplets through a heating zone having a temperature of from about 400° C to about 1700° C.

77. A method as recited in Claim 74, wherein said droplets have a size distribution such that no greater than about 20 weight percent of the droplets in said aerosol are larger than about twice the weight average droplet size.

78. A method as recited in Claim 74, further comprising the step of removing a portion of droplets from said aerosol, said removed droplets having aerodynamic diameter greater than a preselected maximum diameter.

79. A method as recited in Claim 74, further comprising the step of removing a second portion of said droplets from said aerosol, wherein said second portion of droplets have an aerodynamic diameter less than a preselected minimum diameter.

80. A method as recited in Claim 74, wherein said liquid is a solution comprising a oxygen-containing phosphor precursor comprising a metal nitrate.

81. A method as recited in Claim 74, further comprising the step of coating an outer surface of said oxygen-containing phosphor particles.

82. A method as recited in Claim 81, wherein said coating is a metal oxide coating.

83. A method as recited in Claim 81, wherein said coating is an organic coating.

84. A method as recited in Claim 74, wherein said method further comprises the step of annealing said phosphor particles to increase the crystallinity of said particles.

85. A display device for conveying visual graphics and information, comprising:

a) a plurality of pixel regions comprising phosphor powder layers; and

b) an excitation source adapted to stimulate said phosphor powder to emit light to be viewed by a viewer;

wherein said phosphor powder comprises oxygen-containing phosphor particles that are substantially spherical and have a weight average particle size of not greater than about 5 μm.

86. A display device as recited in Claim 85, wherein said weight average particle size is from about 0.3 μm to about 3 μm.

87. A display device as recited in Claim 85, wherein said powder has a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

88. A display device as recited in Claim 85, wherein said phosphor powder layers have an average thickness of not greater than about 3 times said average particle size.

89. A display device as recited in Claim 85, wherein said phosphor powder layers have an average thickness of not greater than about 2 times said average particle size.

90. A display device as recited in Claim 85, wherein said phosphor particles comprise a metal oxide host material selected from the group consisting of ZnO, Y_2O_3, $Y_3Al_5O_{12}$ and $BaMgAl_{14}O_{23}$.

91. A display device as recited in Claim 85, wherein said phosphor particles comprise a silicate host material selected from the group consisting of Zn_2SiO_4, Ca_2SiO_4, Ba_2SiO_4, Gd_2SiO_4 and Y_2SiO_5.

92. A display device as recited in Claim 85, wherein said phosphor particles comprise a borate host material.

93. A display device as recited in Claim 85, wherein said phosphor particles comprise a host material consisting essentially of ZnO.

94. A display device as recited in Claim 85, wherein said phosphor particles comprise a host material consisting essentially of Y_2O_3.

95. A flat panel display, comprising:

a) an excitation source adapted to stimulate a phosphor; and

b) a viewing panel proximate to said excitation source, comprising a transparent substrate having disposed thereon an oxygen-containing phosphor powder defining pixels, wherein said phosphor powder comprises substantially spherical particles having a weight average particle size of not greater than about 10 μm.

96. A flat panel display as recited in Claim 95, wherein said weight average particle size is not greater than about 5 μm.

97. A flat panel display as recited in Claim 95, wherein said weight average particle size is from about 0.3 μm to about 3 μm.

98. A flat panel display as recited in Claim 95, wherein said powder has a particle size distribution wherein at least about 90 weight percent of said particles are not larger than twice said average particle size.

99. A flat panel display as recited in Claim 95, wherein said pixels comprise a phosphor powder layer having an average thickness of not greater than about 3 times said average particle size.

100. A flat panel display as recited in Claim 95, wherein said pixels comprise a phosphor powder layer having an average thickness of not greater than about 2 times said average particle size.

101. A flat panel display as recited in Claim 95, wherein said flat panel display is a field emission display.

102. A flat panel display as recited in Claim 95, wherein said flat panel display is a plasma display.

103. A flat panel display as recited in Claim 95, wherein said phosphor powder comprises a metal oxide host material selected from the group consisting of ZnO, Y_2O_3, $Y_3Al_5O_{12}$ and $BaMgAl_{14}O_{23}$.

104. A display device as recited in Claim 95, wherein said phosphor particles comprise a silicate host material selected from the group consisting of Zn_2SiO_4, Ca_2SiO_4, Ba_2SiO_4, Gd_2SiO_4 and Y_2SiO_5.

105. A display device as recited in Claim 95, wherein said phosphor particles comprise a borate host material.

106. A display device as recited in Claim 95, wherein said phosphor particles comprise a host material consisting essentially of ZnO.

107. A display device as recited in Claim 95, wherein said phosphor particles comprise a host material consisting essentially of Y_2O_3.

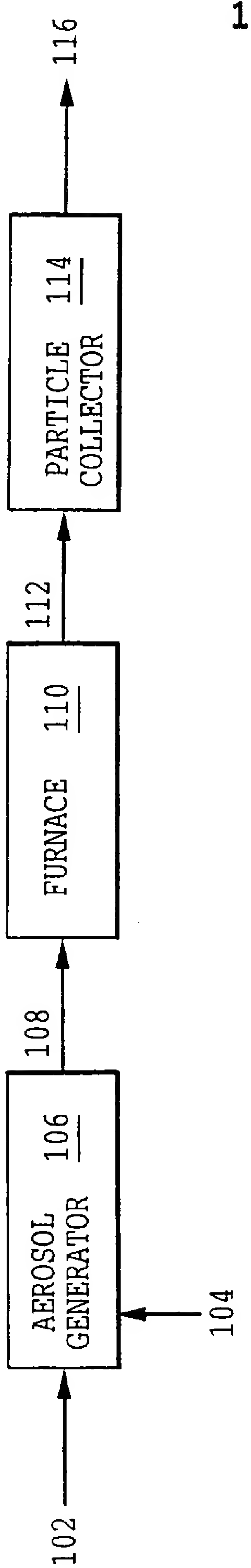
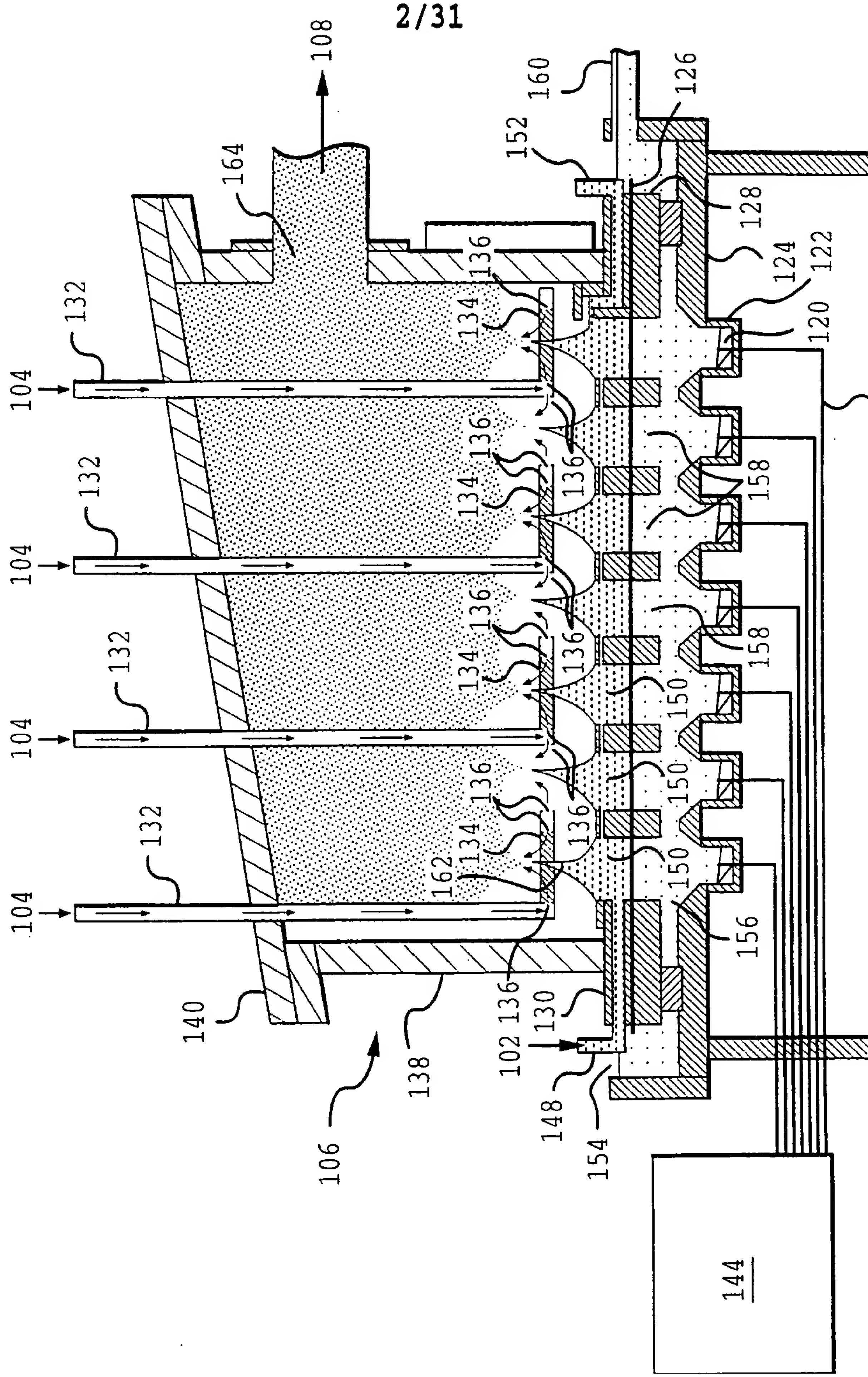

102
104
AEROSOL GENERATOR 106
108
FURNACE 110
112
PARTICLE COLLECTOR 114
116

FIG.1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144

FIG.2

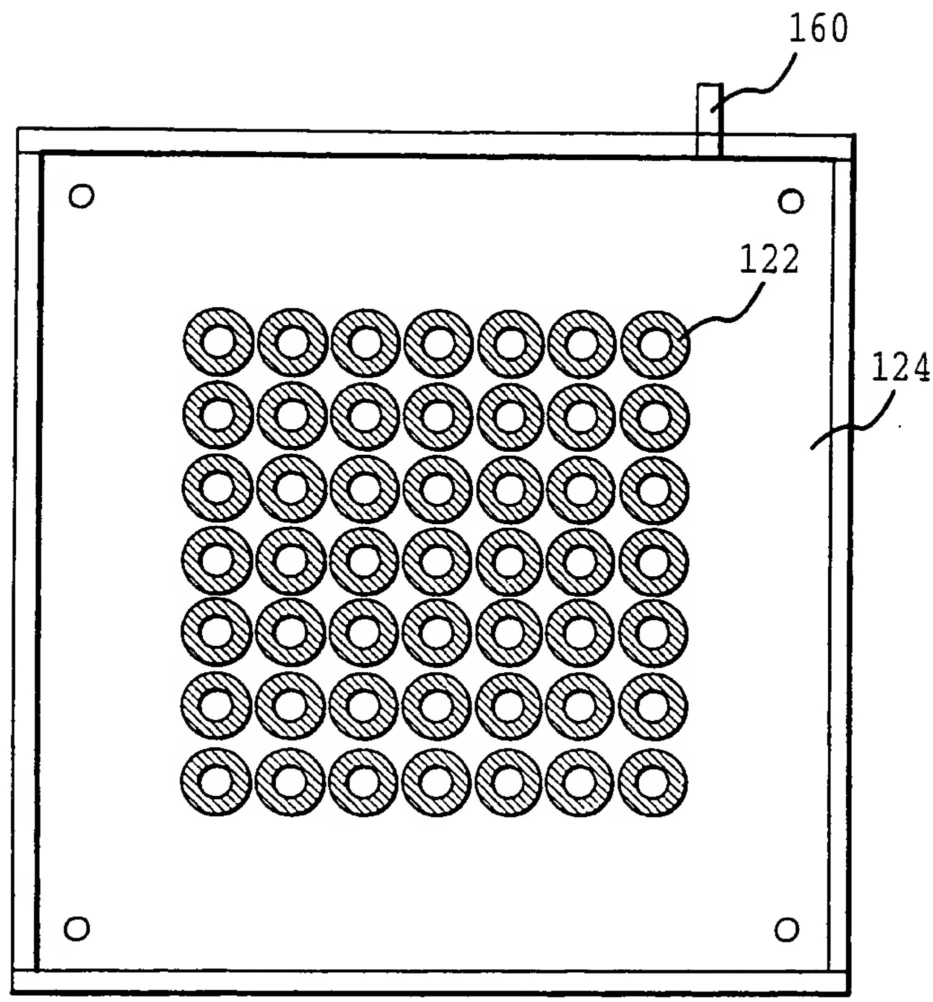


FIG.3

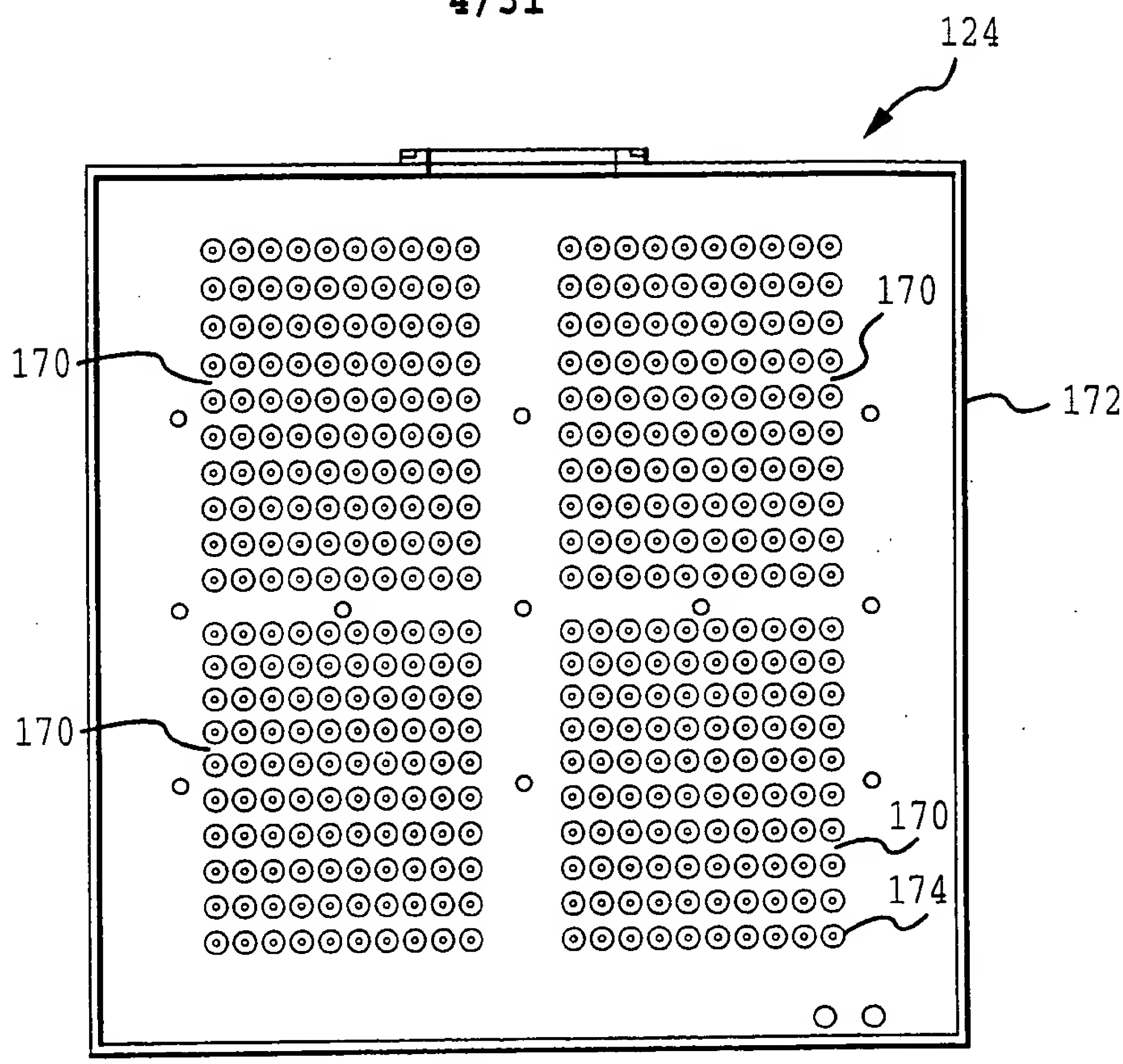


FIG.4

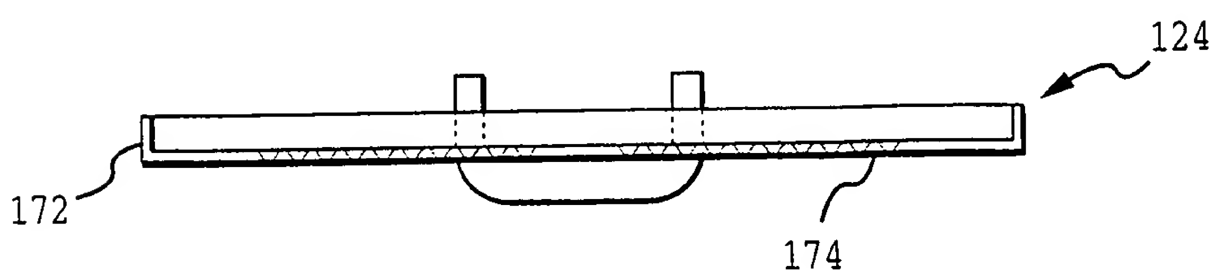


FIG.5

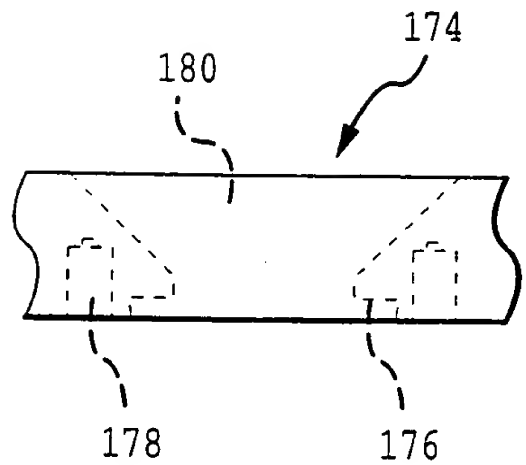


FIG.6

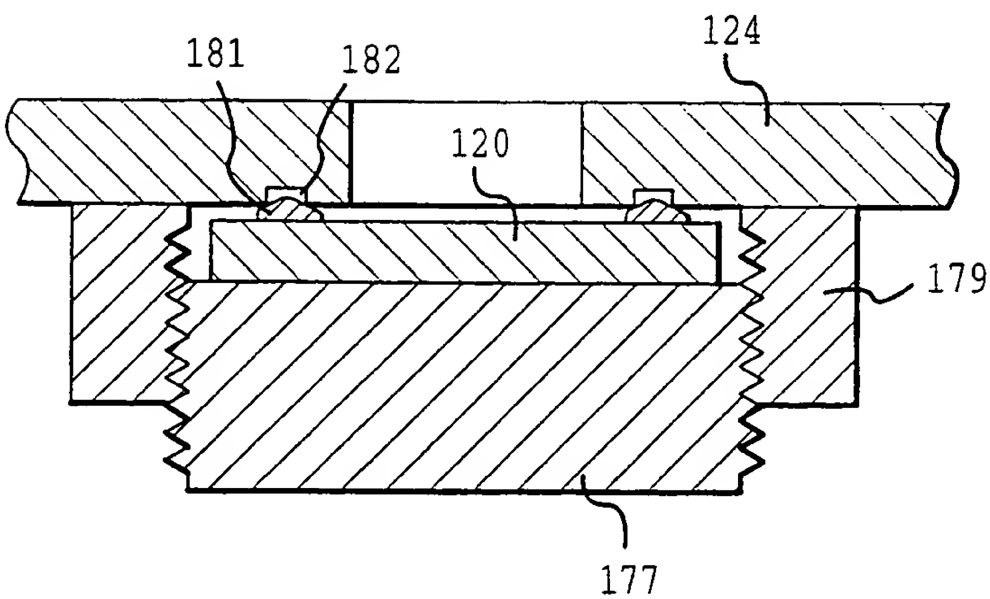


FIG.7

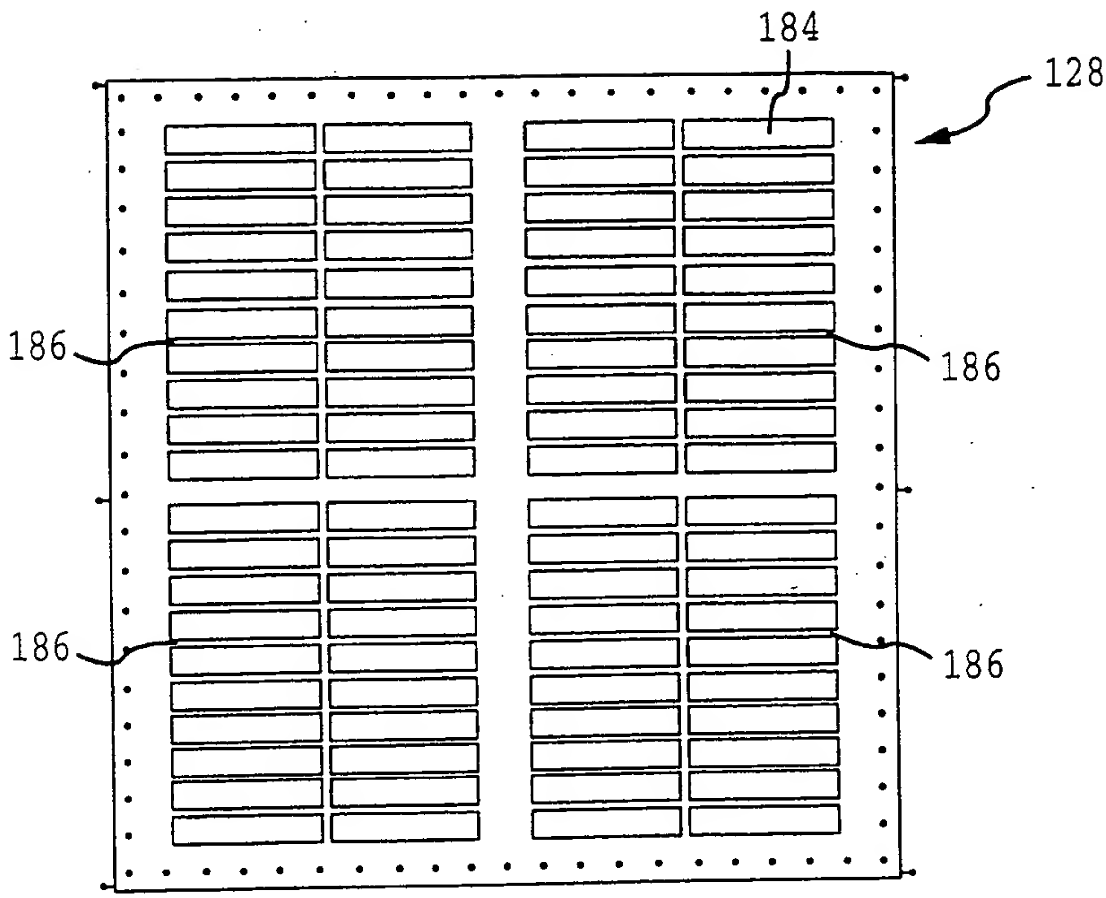


FIG.8

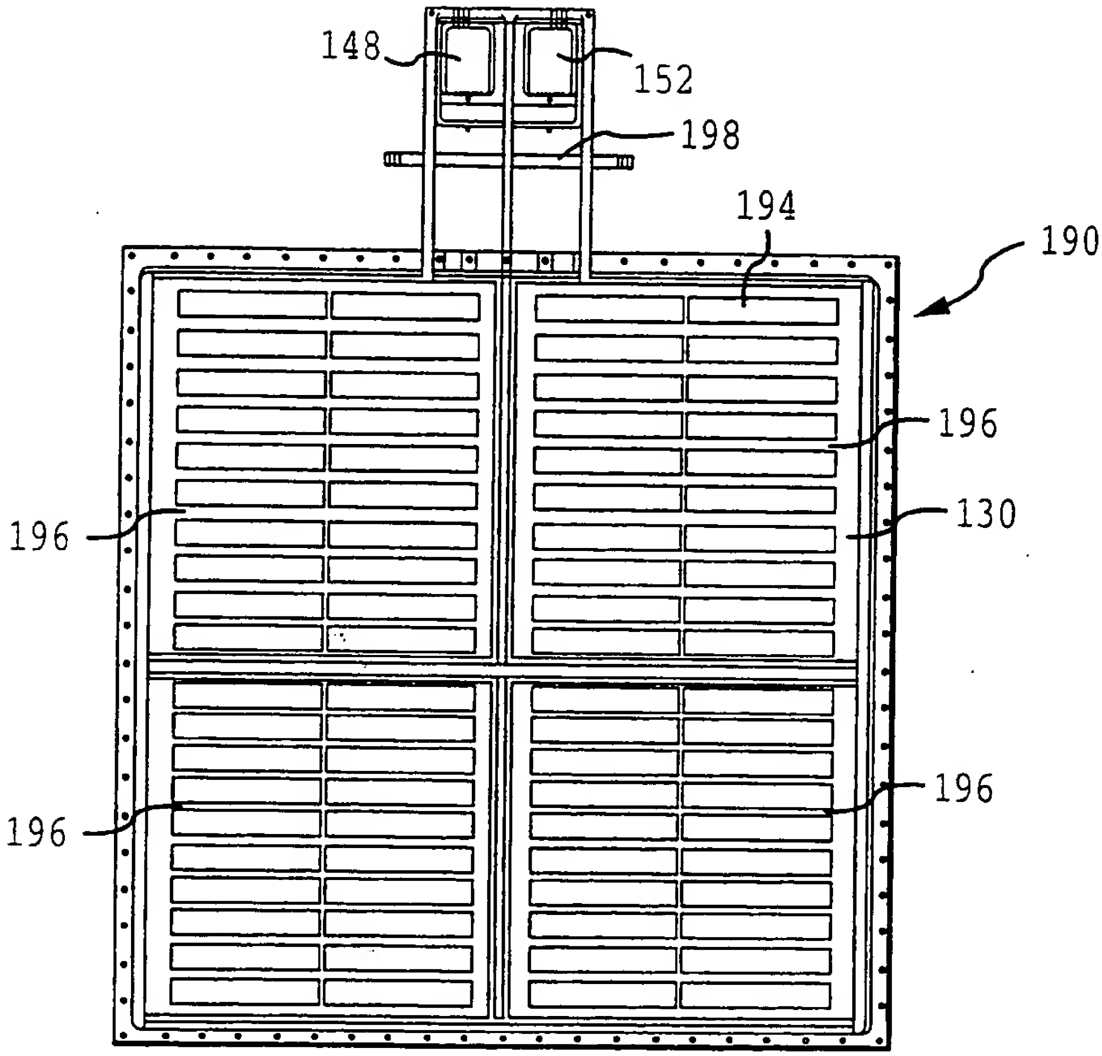


FIG.9

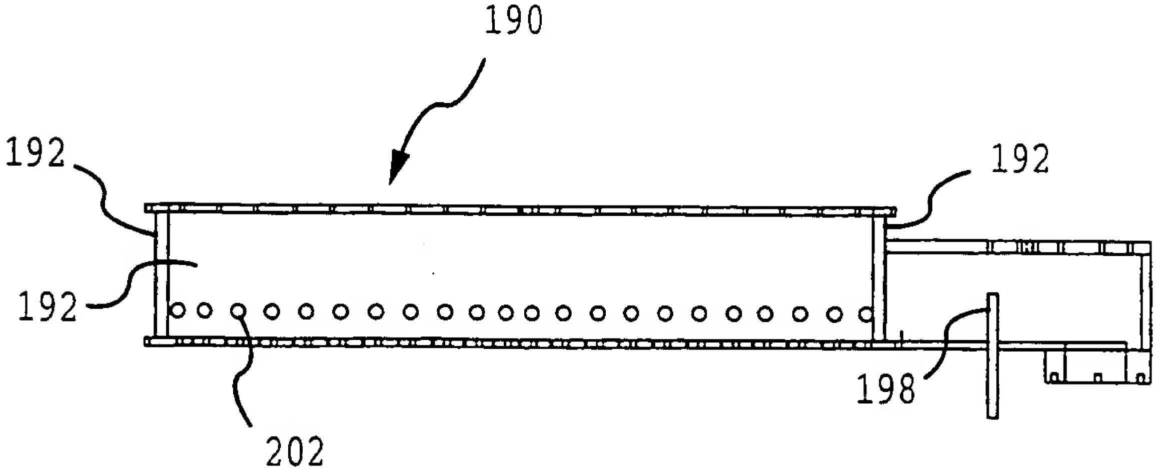


FIG.10

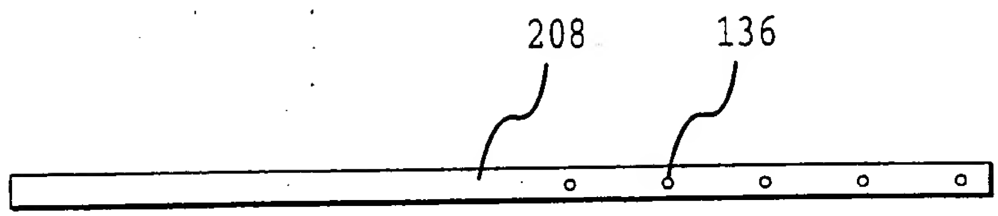


FIG.11

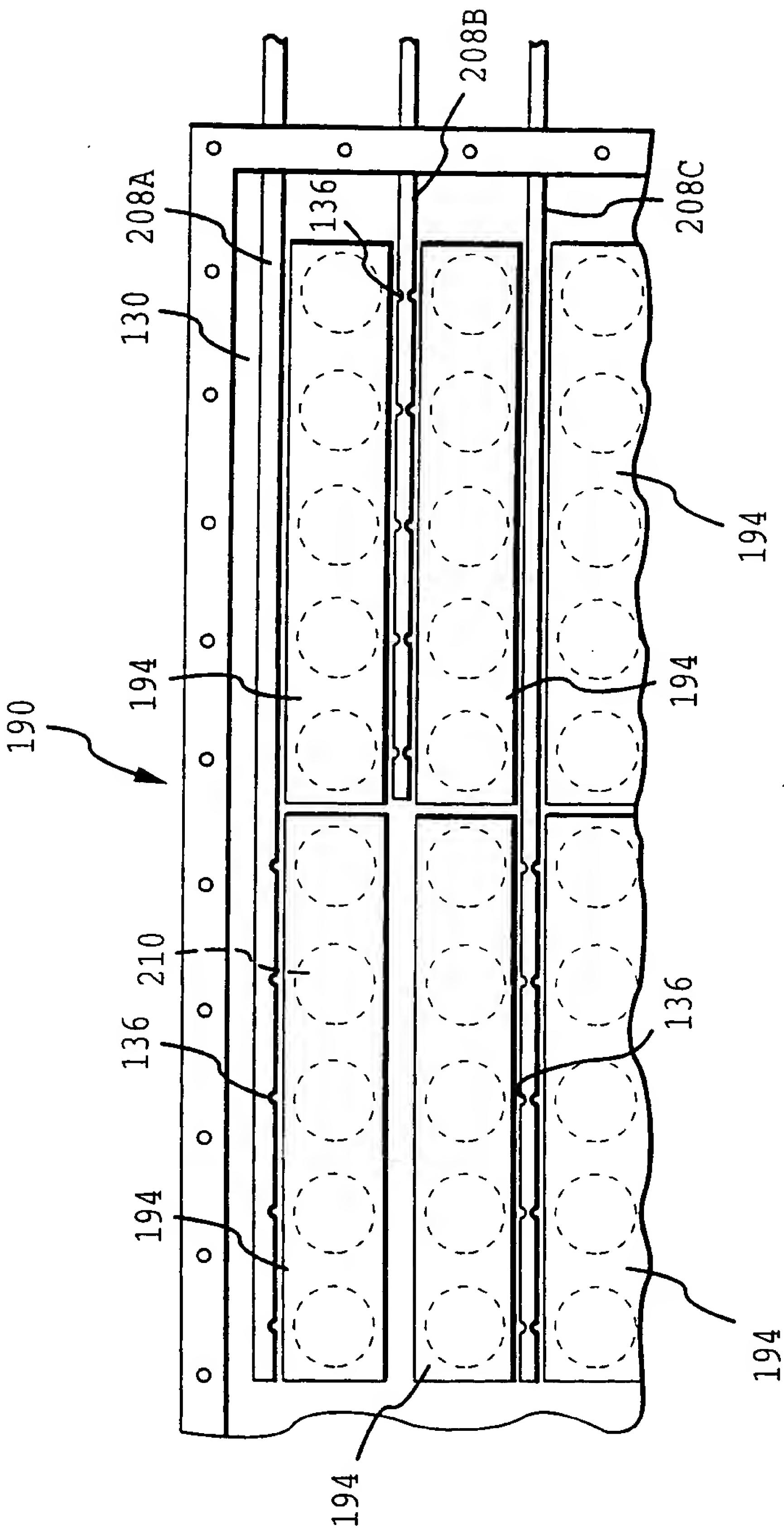


FIG.12

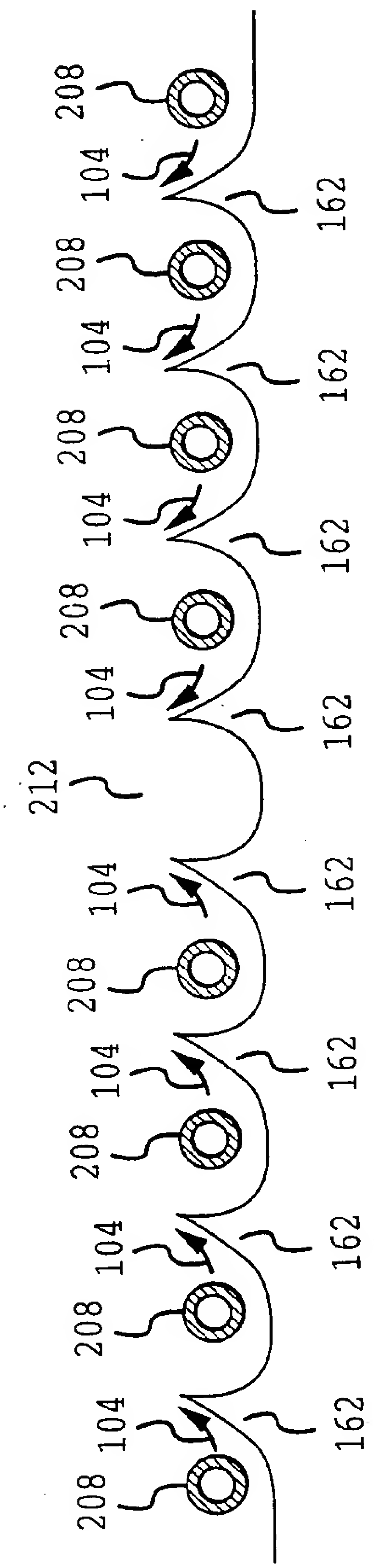


FIG.13

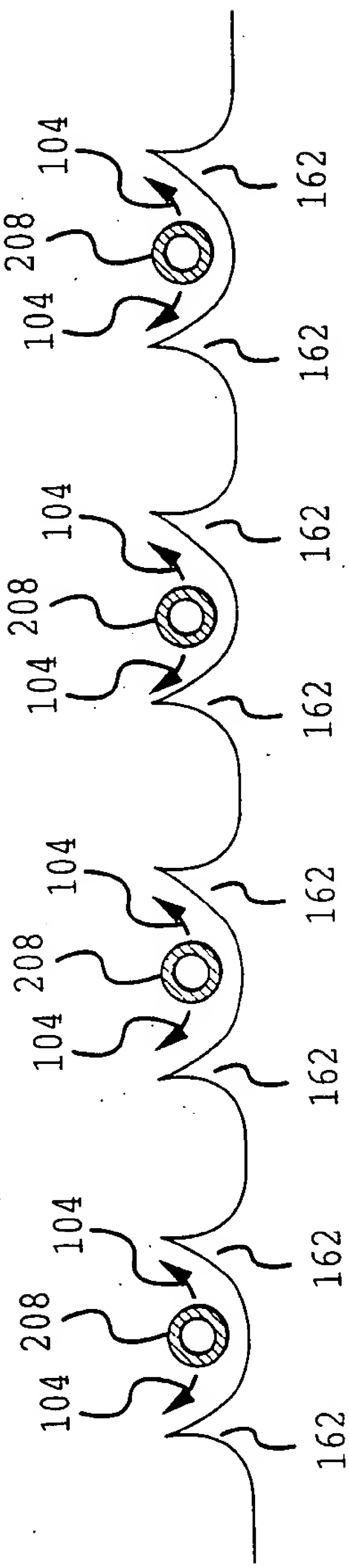


FIG.14

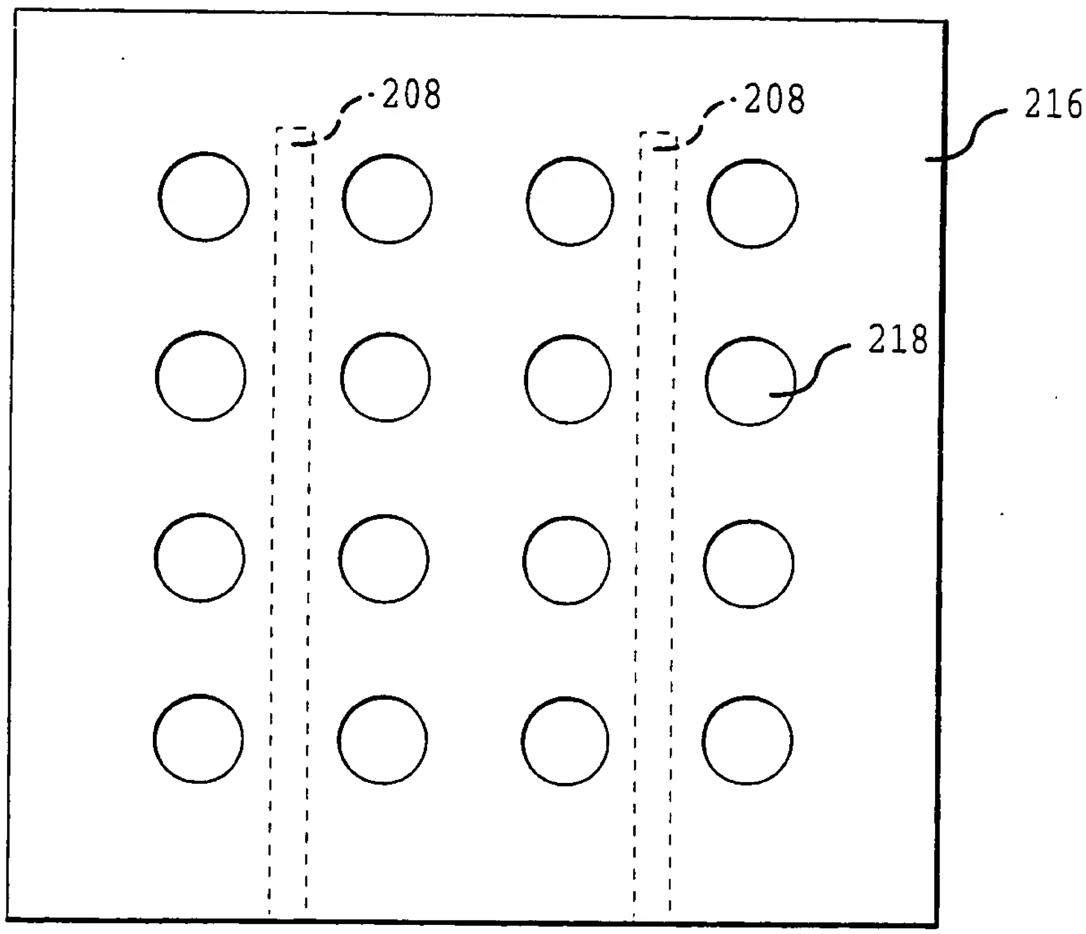
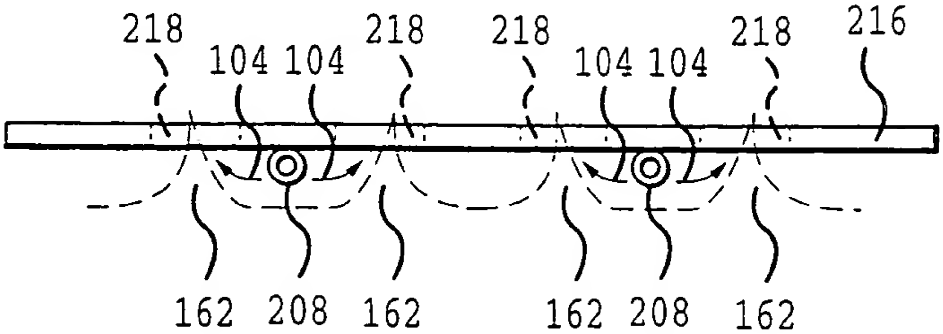

208
208
216
218

FIG.15


218
104 104
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104 104
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162
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162

FIG.16

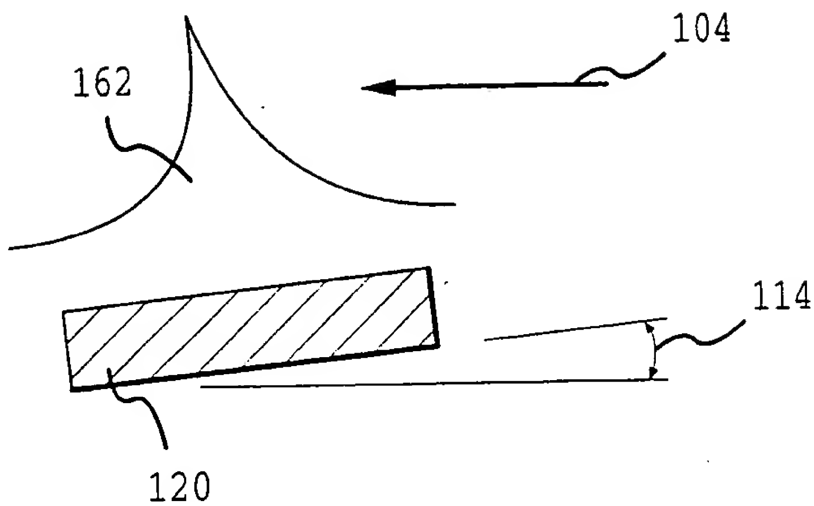


FIG.17

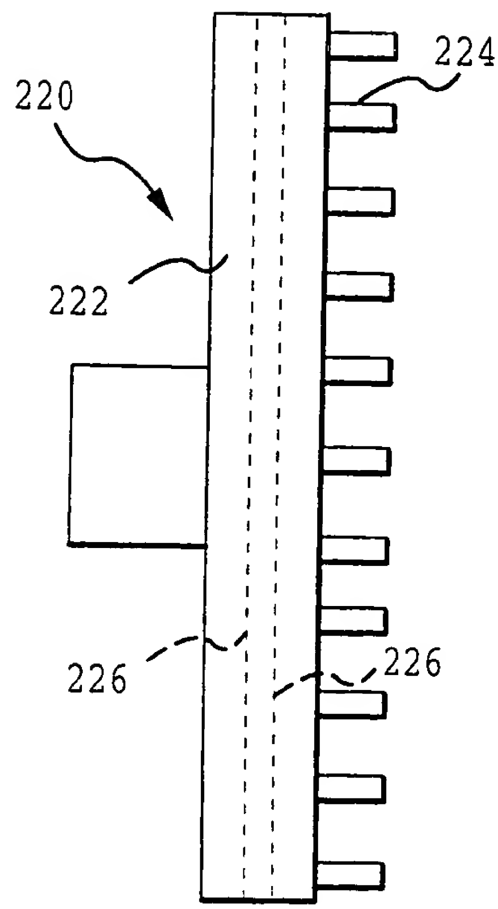


FIG.18

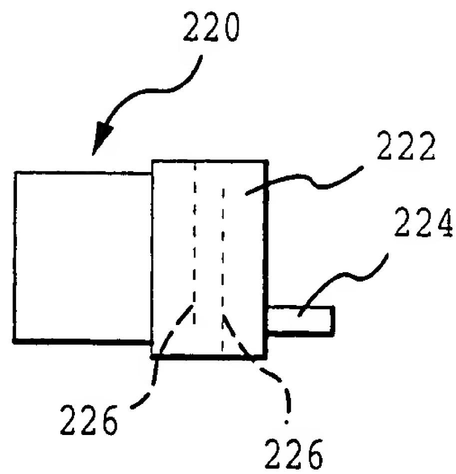


FIG.19

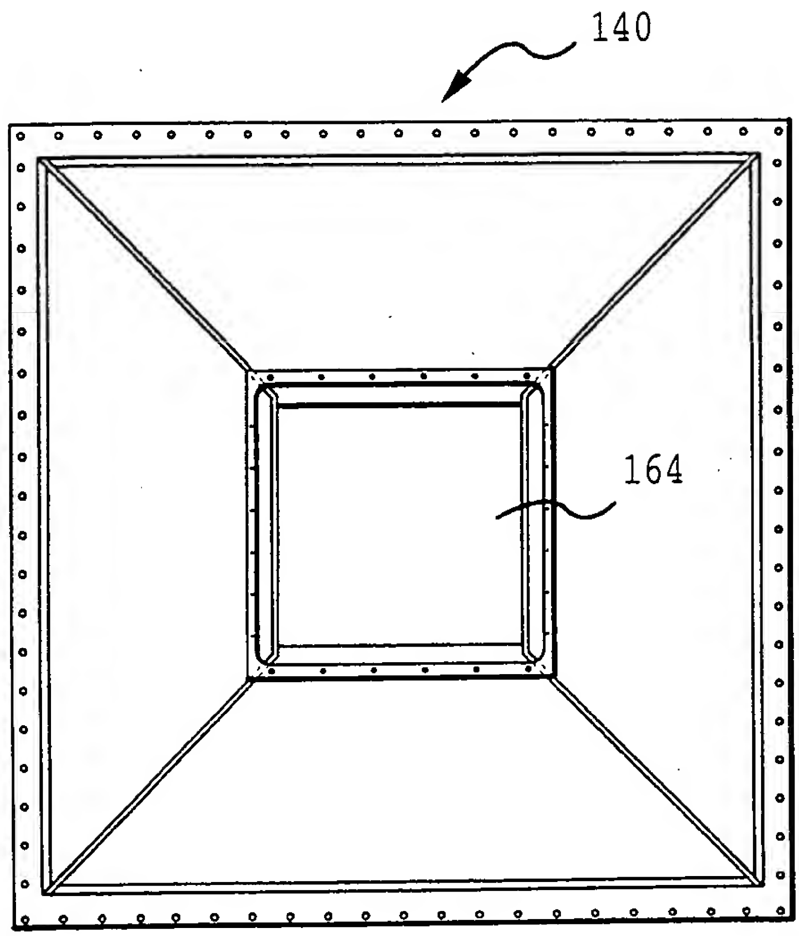


FIG.20

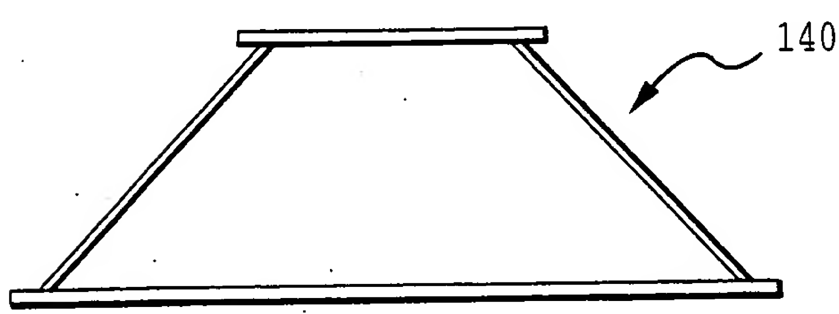
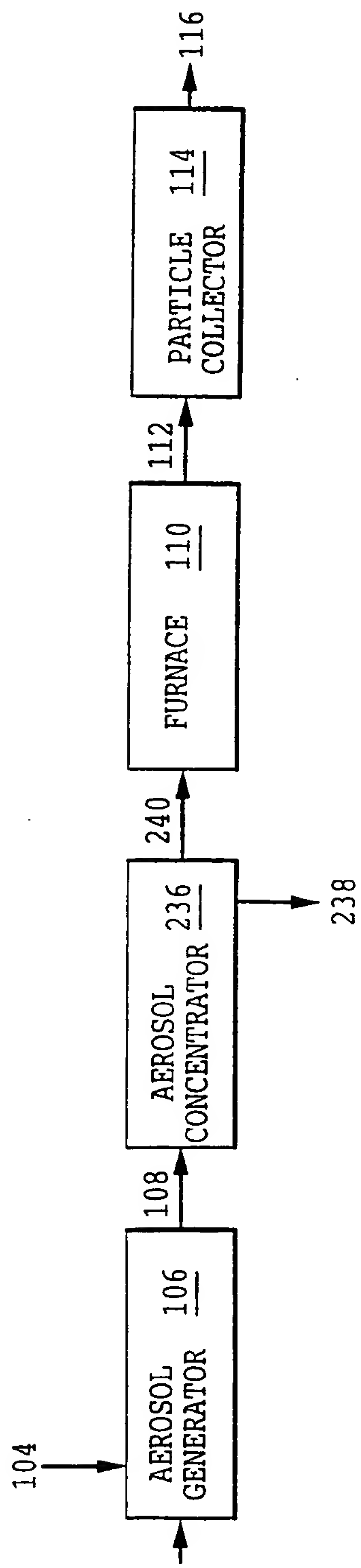


FIG.21


104
AEROSOL GENERATOR 106
108
AEROSOL CONCENTRATOR 236
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240
FURNACE 110
112
PARTICLE COLLECTOR 114
116

FIG.22

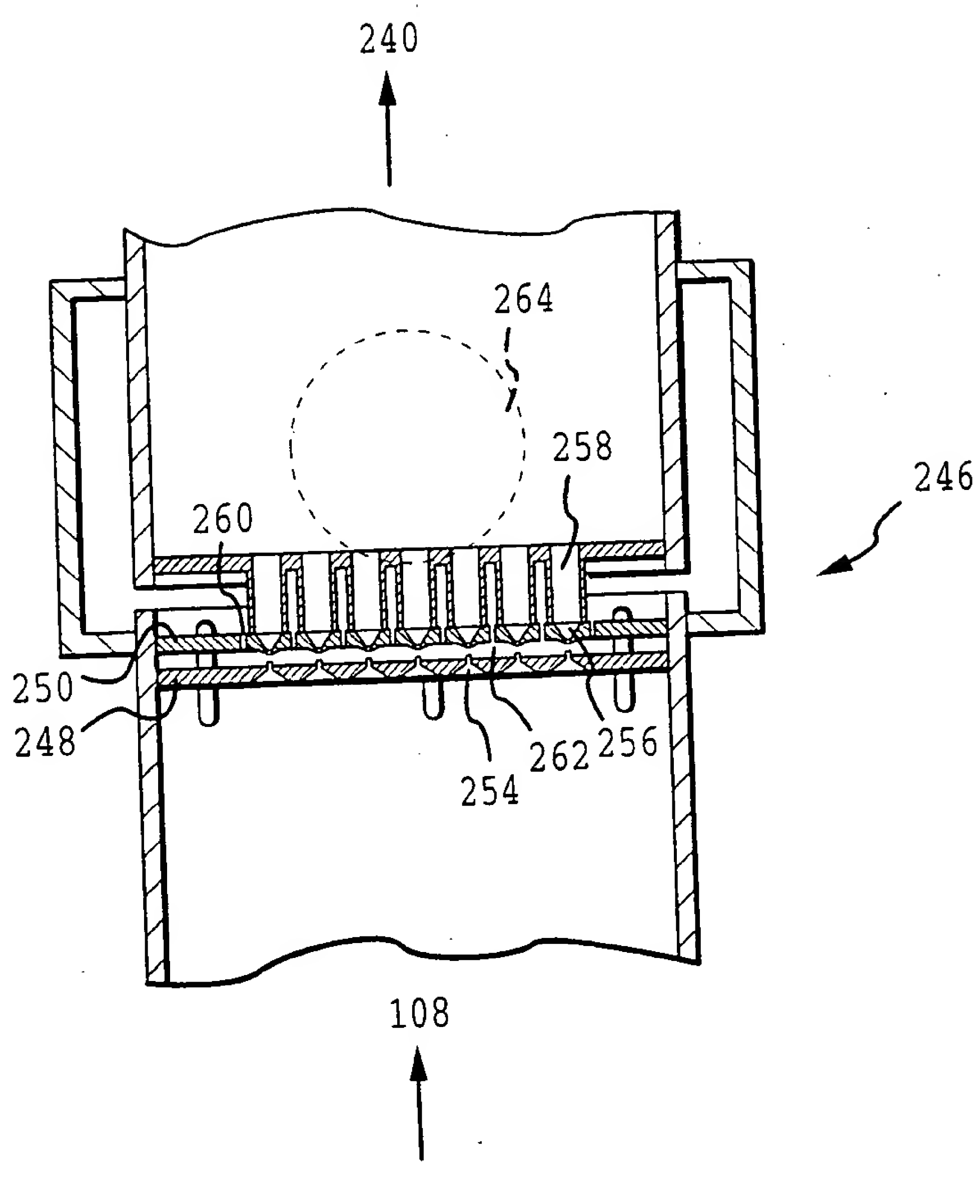


FIG.23

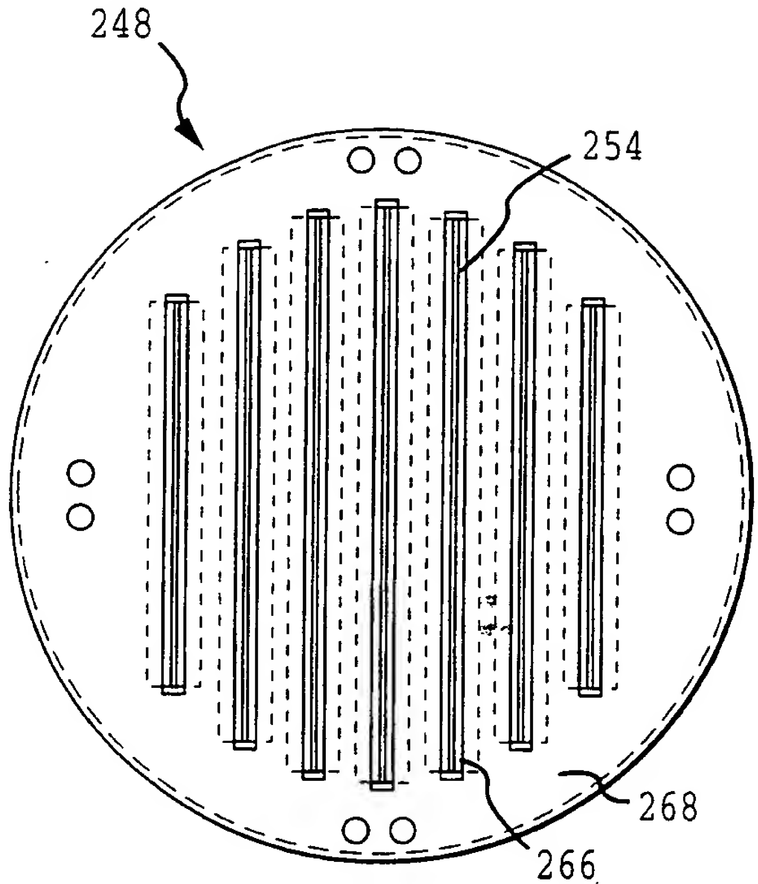


FIG.24

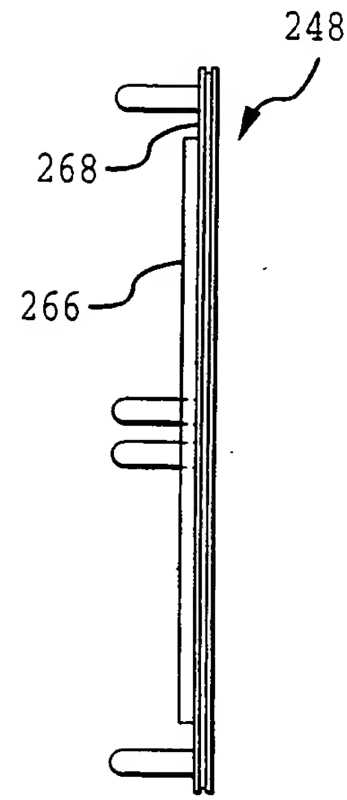


FIG.26

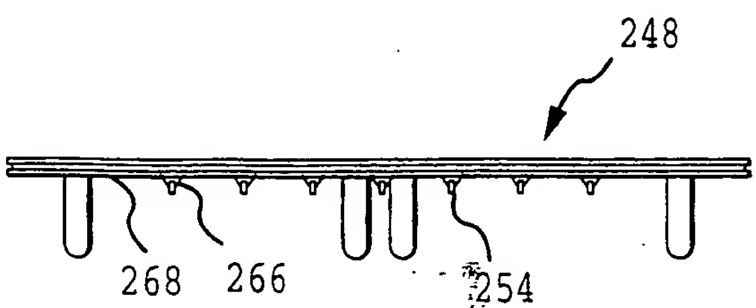


FIG.25

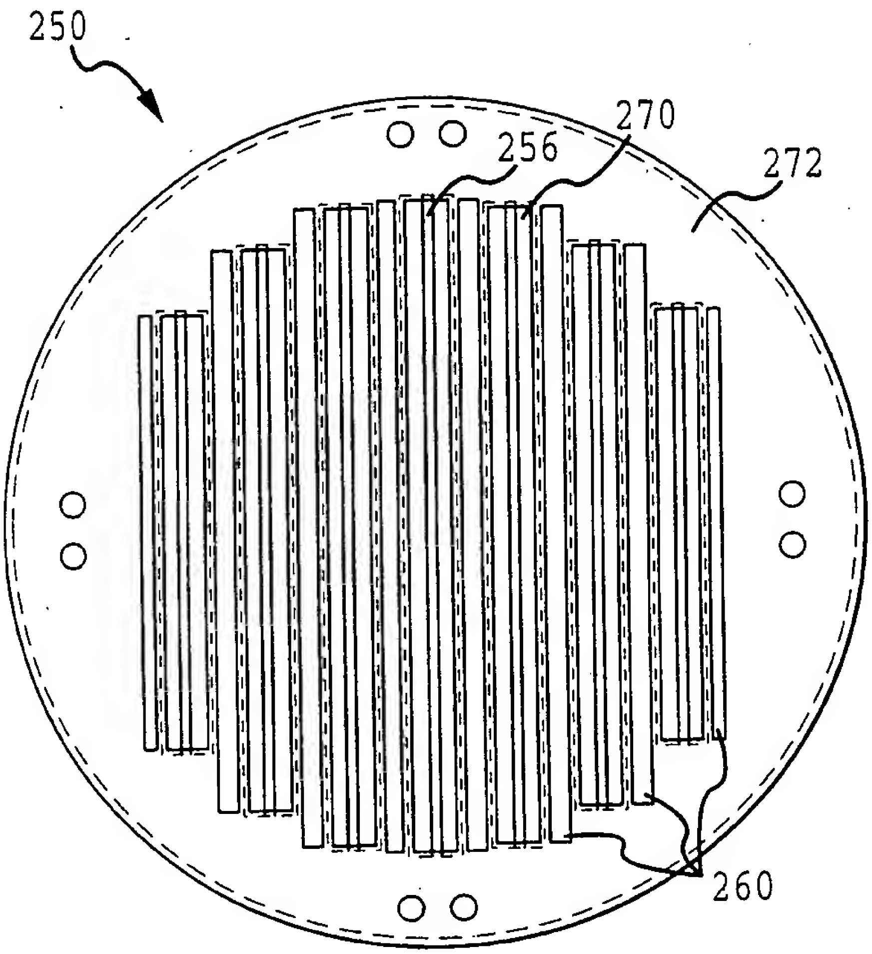


FIG.27

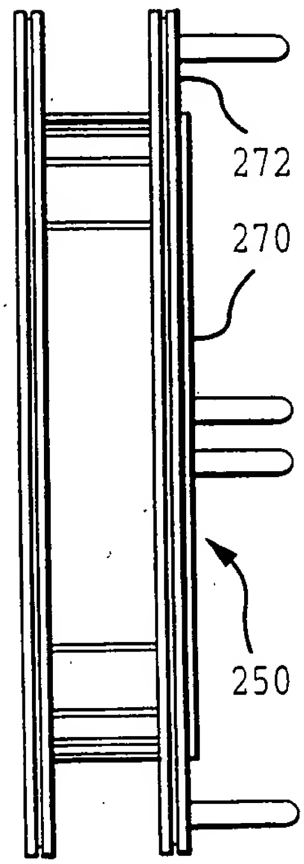


FIG.29

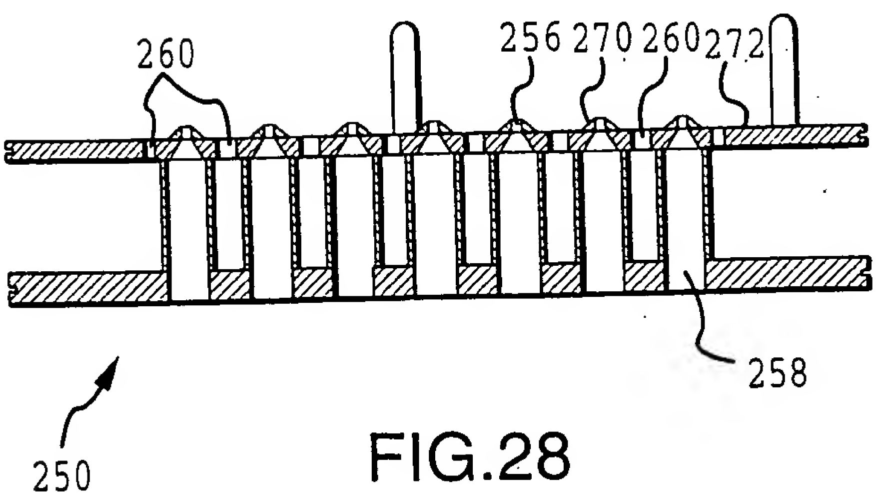
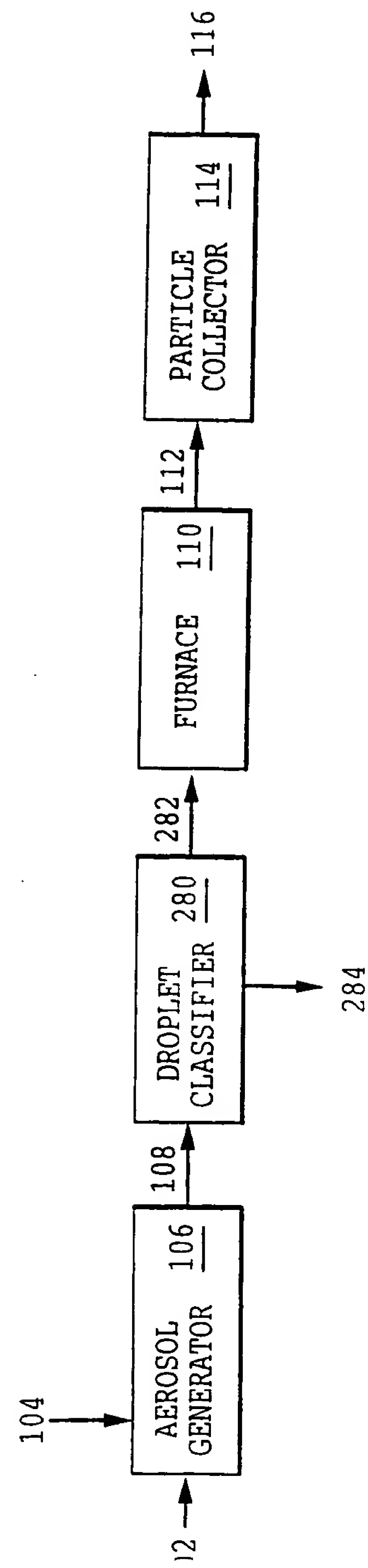


FIG.28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DROPLET CLASSIFIER 280
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FURNACE 110
112
PARTICLE COLLECTOR 114
116

FIG.30

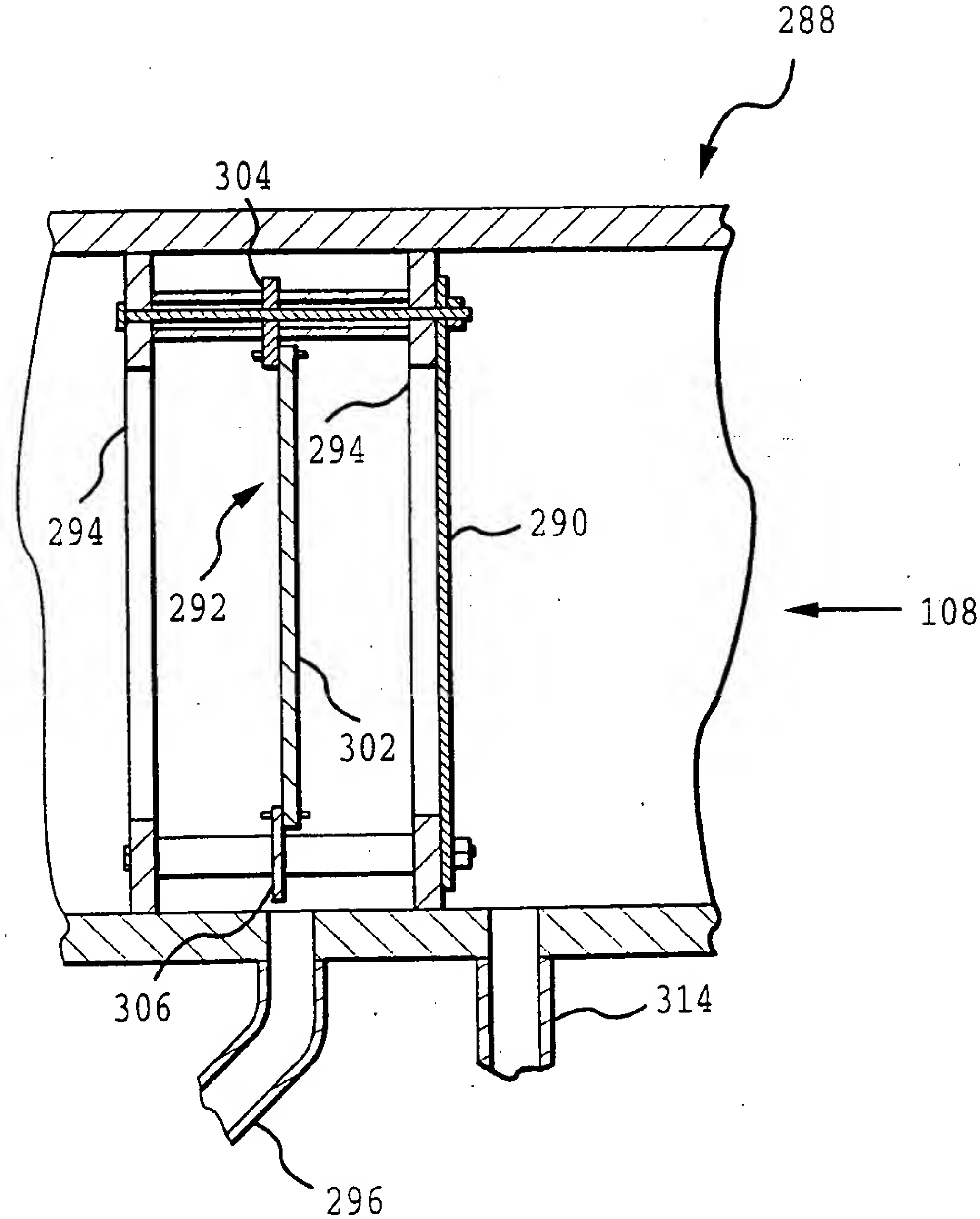

FIG.31

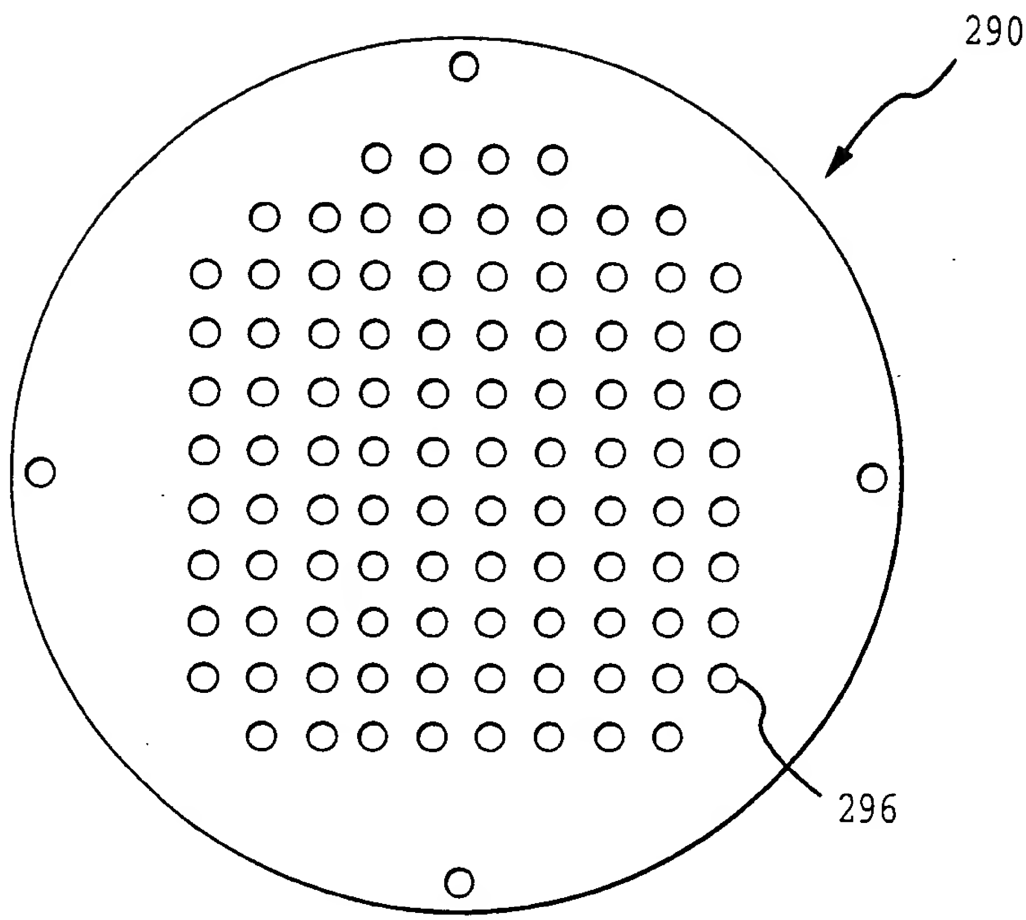

FIG.32

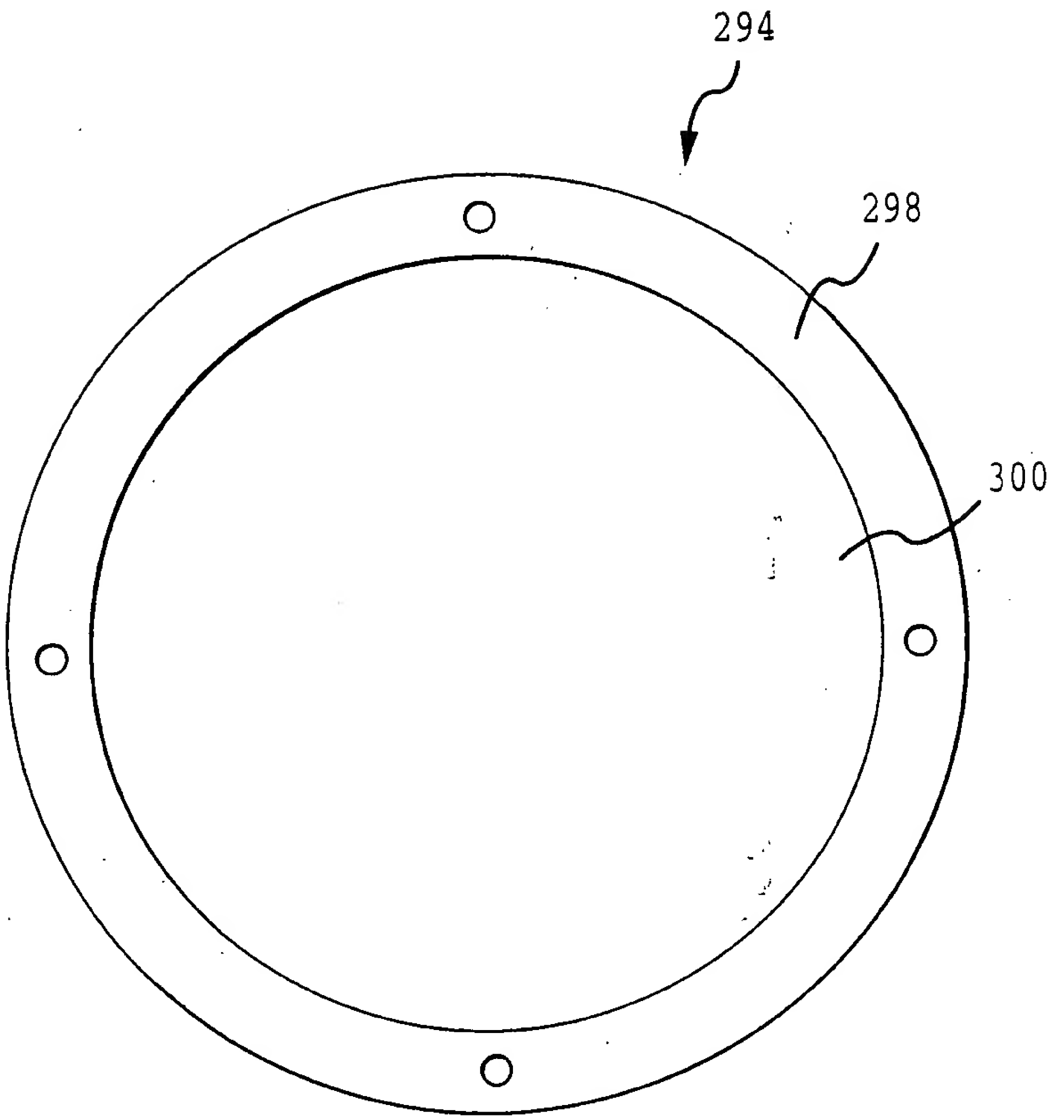

FIG.33

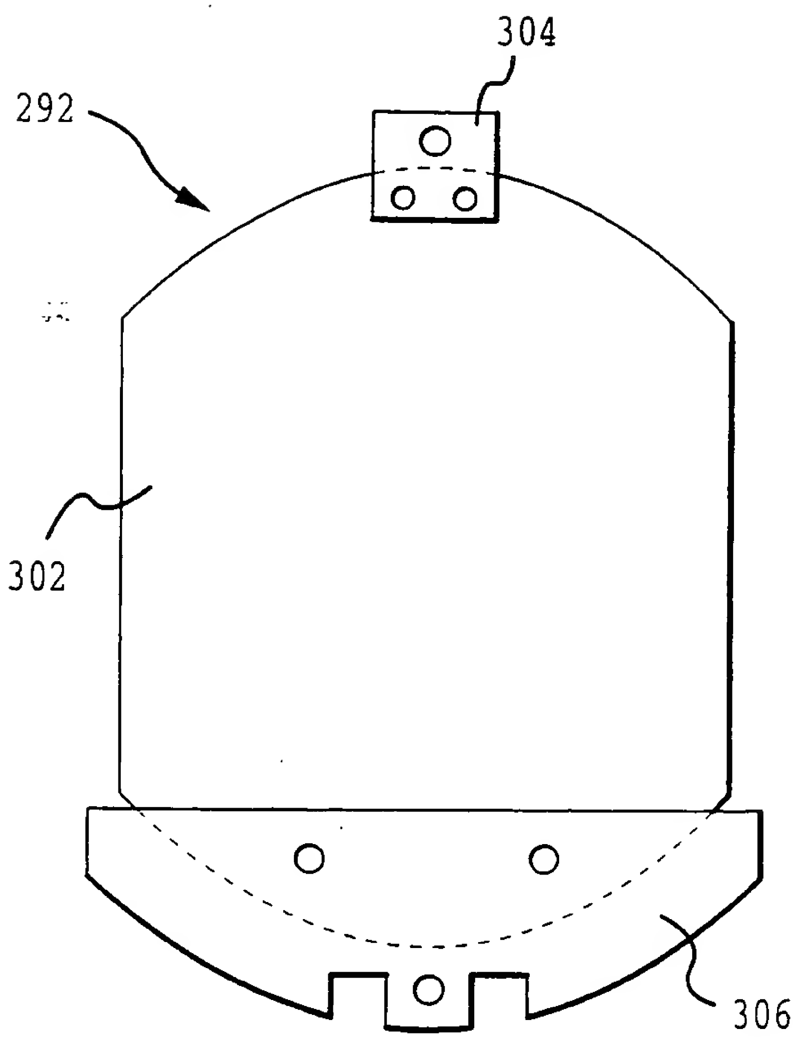

FIG.34

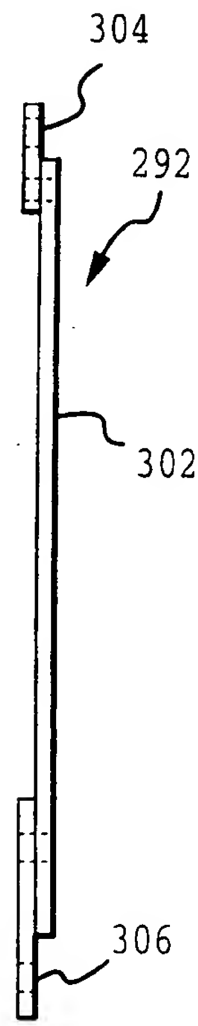

FIG.35

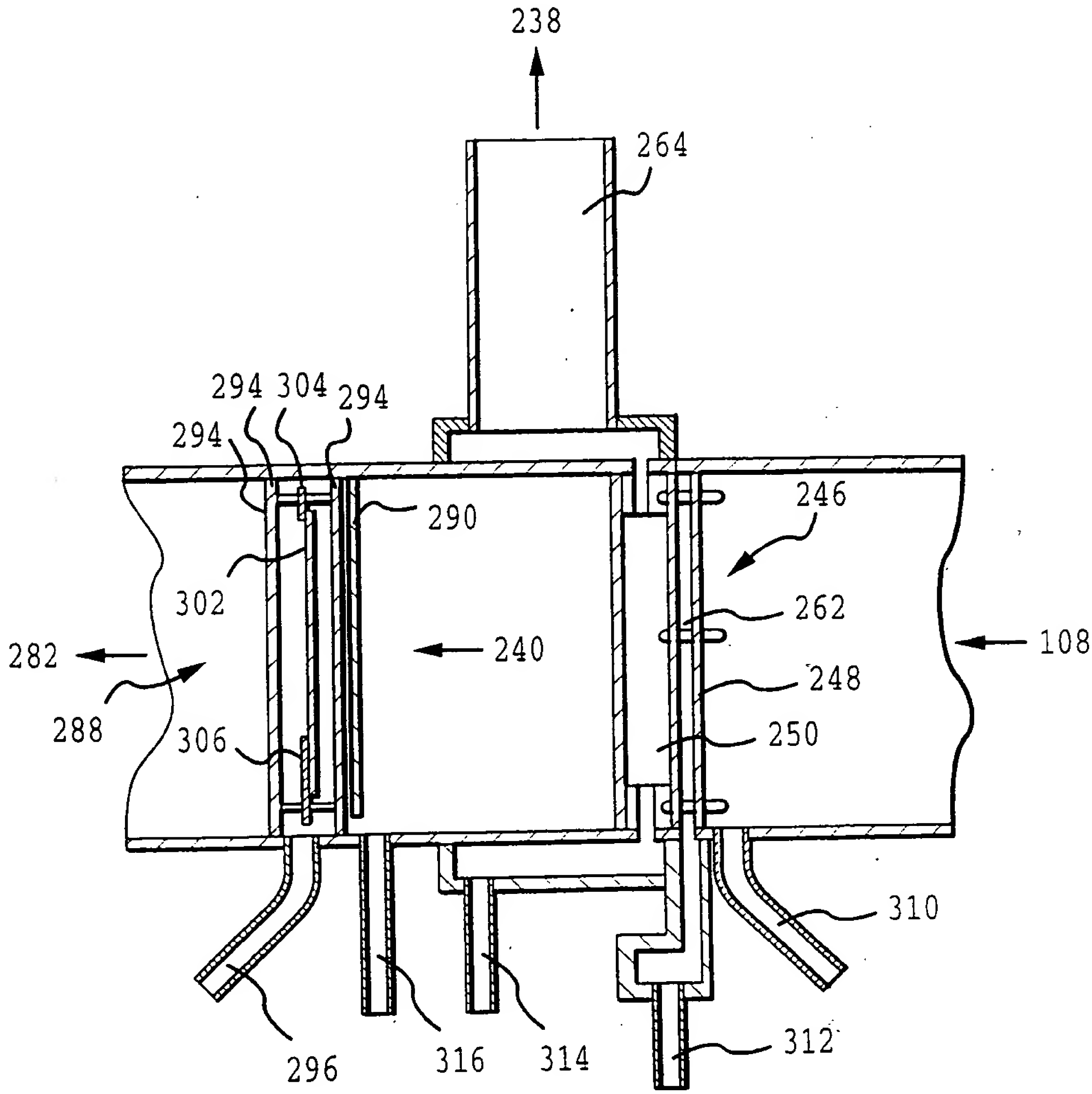
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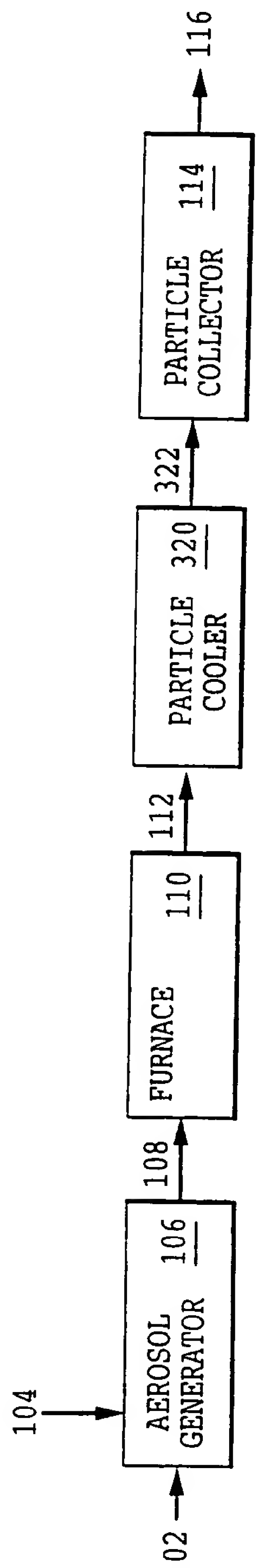
FIG.36


02
104
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108
FURNACE 110
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PARTICLE COOLER 320
322
PARTICLE COLLECTOR 114
116

FIG.37

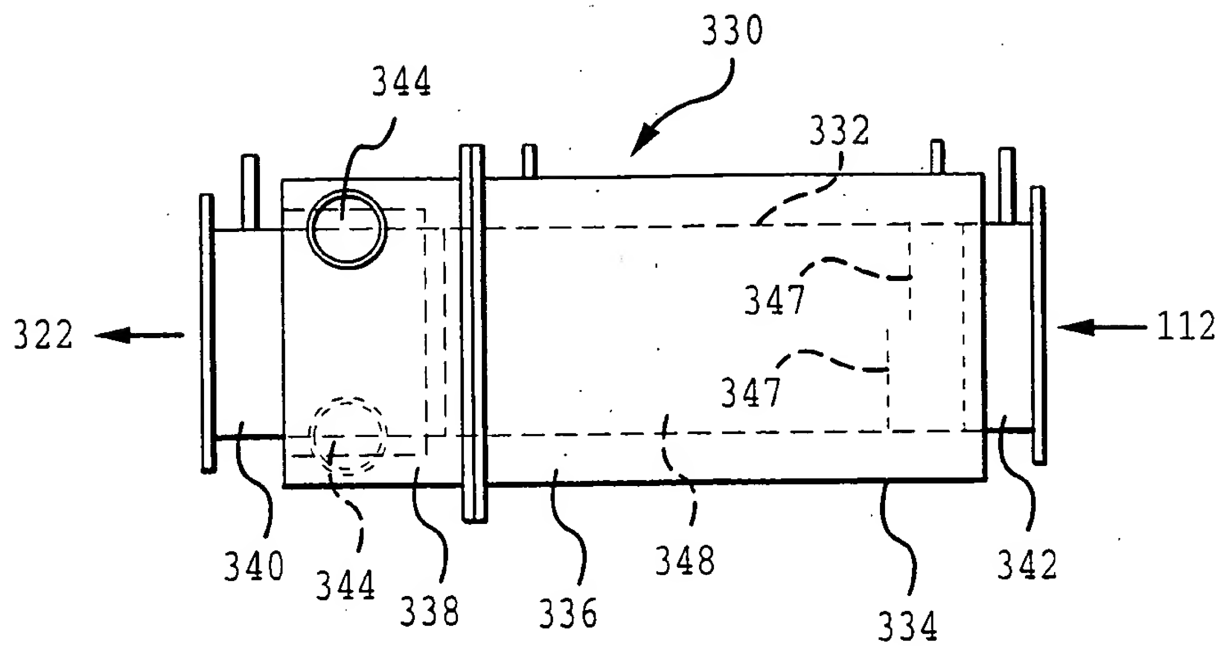


FIG.38

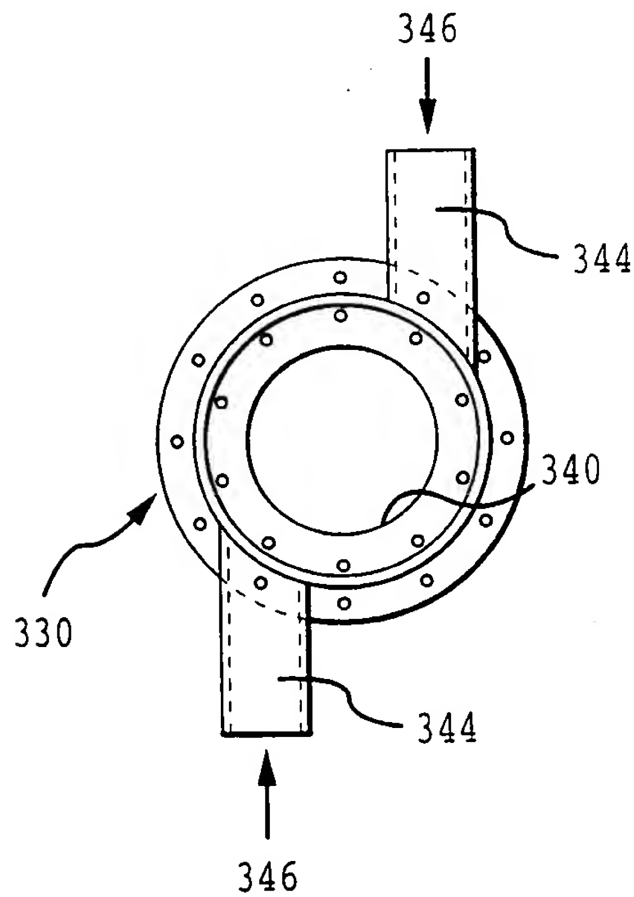


FIG.39

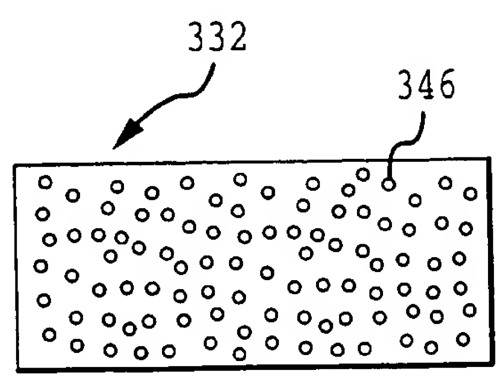
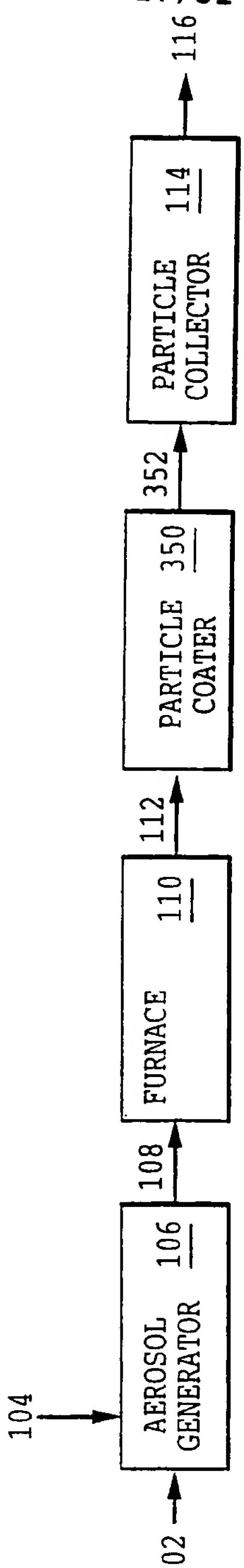


FIG.40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FURNACE 110
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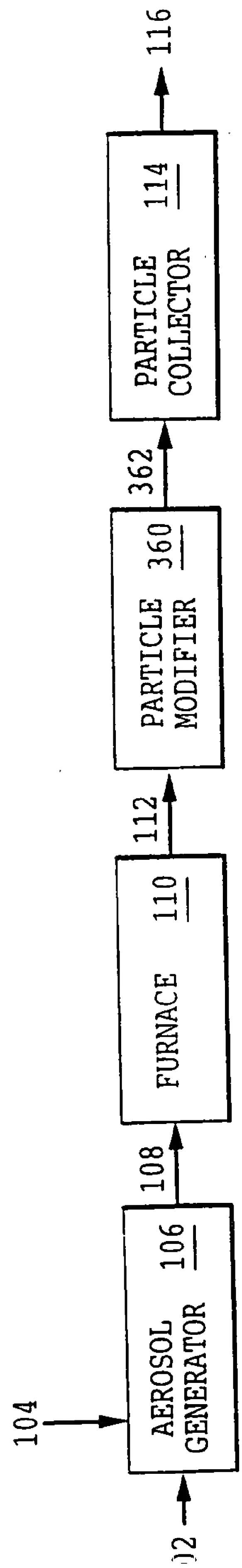
PARTICLE COATER 350
352
PARTICLE COLLECTOR 114
116

FIG.41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FURNACE 110
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PARTICLE MODIFIER 360
362
PARTICLE COLLECTOR 114
116

FIG.42

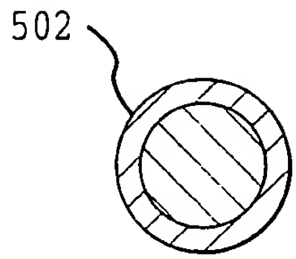

FIG.43a

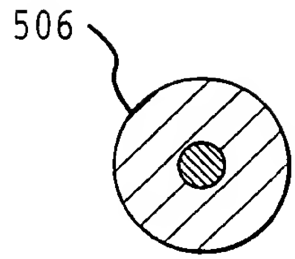

FIG.43b

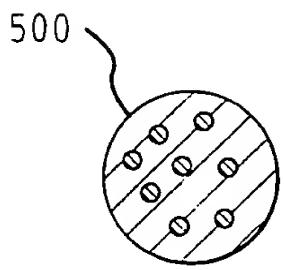

FIG.43c

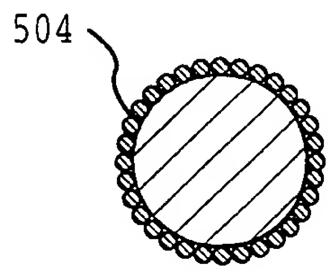

FIG.43d

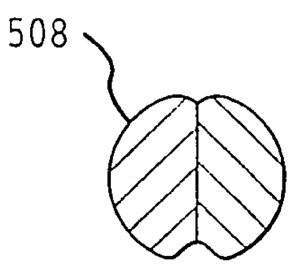

FIG.43e

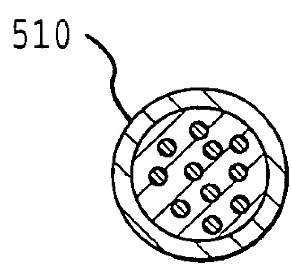

FIG.43f

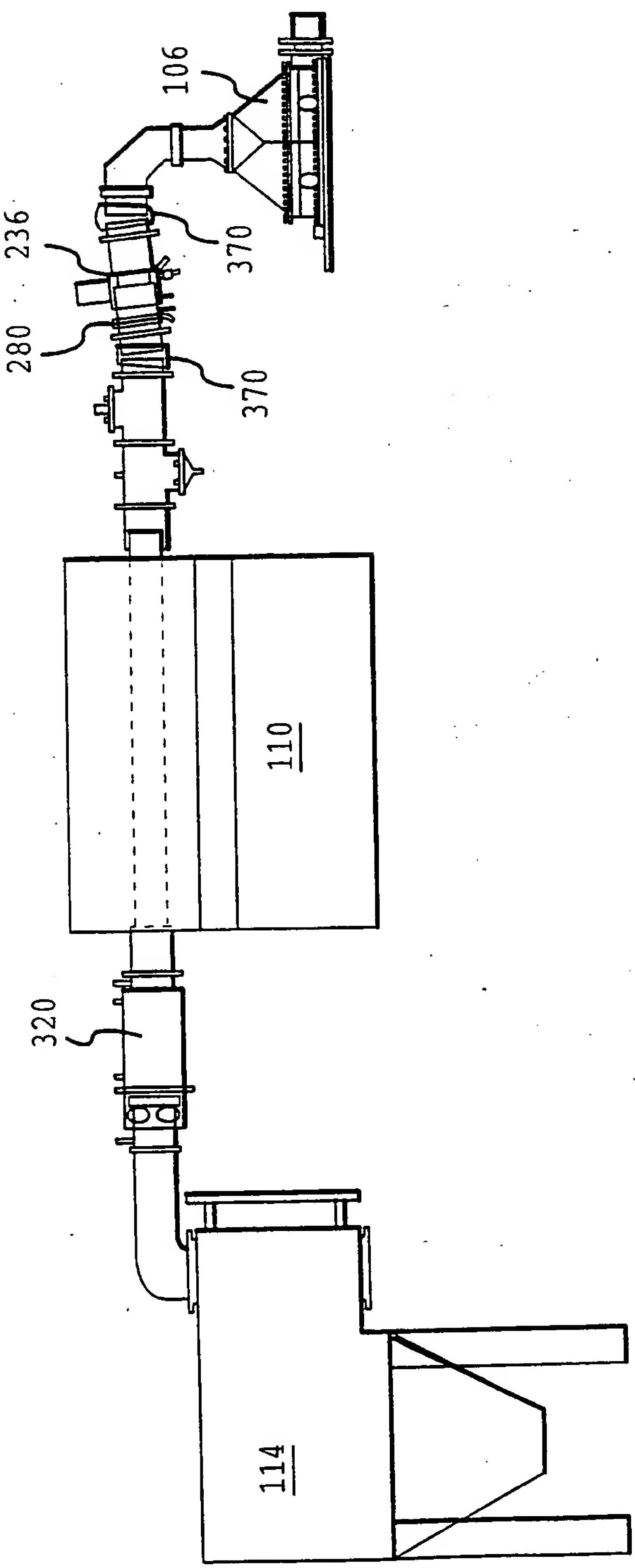

FIG.44

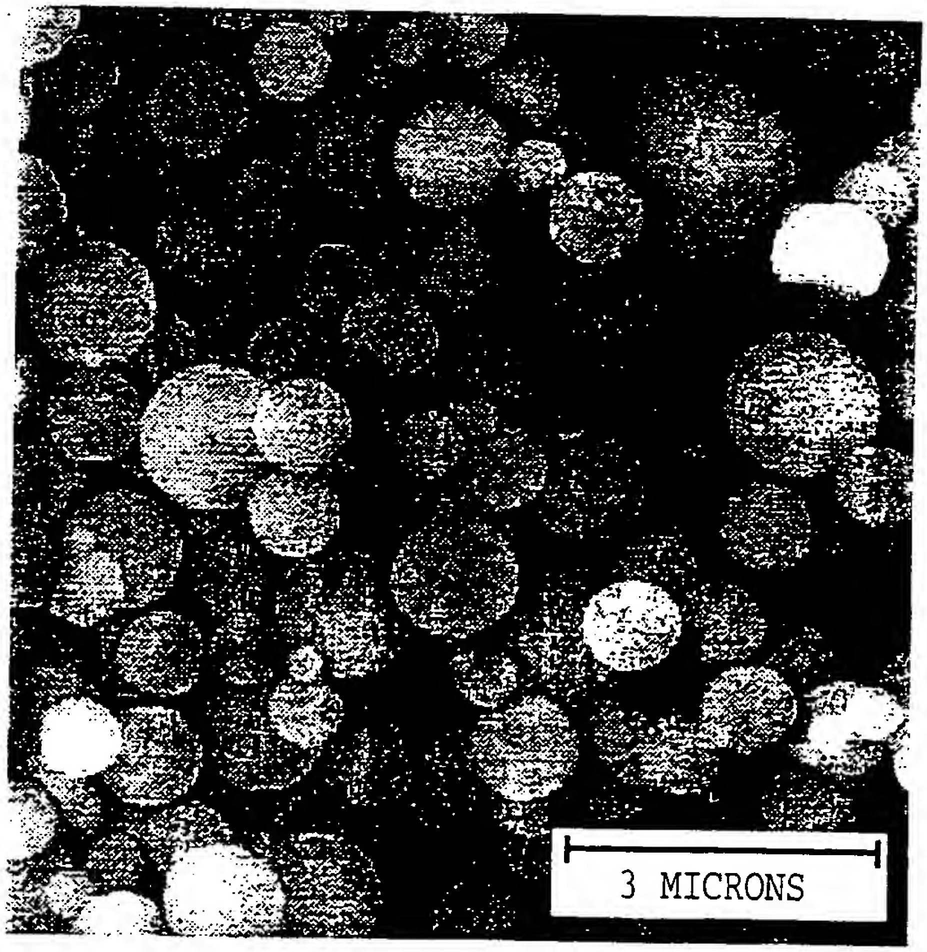

FIG.45

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03566

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/472, 468, 467, 485, 503; 428/404, 403; 252/301.4R, 301.4F, 301.6R, 301.6F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,037,577 A (YAMANOI et al) 06 August 1991 (06-08-91), example 1.	1-5, 12, 13, 15, 16, 18, 33-36, 38, 39
Y, P	US 5,619,098 A (TOKI et al) 08 April 1997 (08-04-97), column 2, line 30-column 8, line 64.	1-4, 9, 12, 13, 15-18, 85-89, 95-102
Y	US 4,309,481 A (WAKATSUKI et al) 05 January 1982 (05-01-82), column 2, line 25-column 10, line 15.	19,56-58, 60-61, 64-65, 67-70, 73
Y	4,287,229 A (WATANABE et al) 01 September 1981 (01-09-81), column 1, line 51-column 6, line 66.	19,56-59, 61, 62, 64-65, 68-70

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search

15 JUNE 1998

Date of mailing of the international search report

08 JUL 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT

Authorized officer

C. MELISSA BONNER

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03566

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US 5,695,685 A (CHAU) 09 December 1997 (09-12-97), column 2, line 20-column 12, line 9.	19, 56-59, 61-62, 64-65, 69-71
Y	US 4,515,827 A (DODDS et al) 07 May 1985 (07-05-85), column 2, line 21-column 4, line 66.	19, 56-59, 61, 62, 64-70
X, P ---- Y, P	US 5,662,831 A (CHADHA) 02 September 1997 (02-09-97), column 2, line 15-column 10, line 4.	1-5, 11-16, 26-29, 31, 32 ---- 17, 30, 85-90, 94-103, 107
Y, P	US 5,611961 A (FORSTER et al) 18 March 1997 (18-03-97), column 2, line 22-column 6, line 28.	1-4, 5, 12, 13, 15-18, 48-55, 85-89, 91
Y	US 5,472,636 A (FORSTER et al) 05 December 1995 (05-12-95), column 2, line 15-column 8, line 56.	1-4, 6, 12, 13,15-18, 48-55, 85-89, 91, 95-100, 104
X ---- Y	US 5,413,736 A (NISHISU et ai) 09 May 1995 (09-05-95), column 1, line 40-column 4, line 52.	1-5, 11-18, 26-32 ---- 85-90, 94-103, 107
Y	US 5,055,226 A (YANG) 08 October 1991 (08-10-91), column 1, line 27-column 4, line 6.	1-5, 11-18, 26-32, 53, 65, 73, 85-90, 94-103, 107
Y	US 5,128,063 A (KAMIKUBO) 07 July 1992 (07-07-92), column 1, line 58-column 4, line 37.	1-5, 10, 12, 13, 15-25, 56-58, 60. 64-65, 69-70, 85--90, 93, 95-103, 106

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03566

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

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A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C09K 11/08, 11/78, 11/54, 11/59, 11/63; H01J 29/18, 1/62; B32B 5/16

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

313/472, 468, 467, 485, 503; 428/404, 403; 252/301.4R, 301.4F, 301.6R, 301.6F

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

ZnO based phosphors
Y_2O_3 based phosphors
$Y_3Al_5O_{12}$ based phosphors
Barium aluminate based phosphors
Metal silicate based phosphors

The claims are deemed to correspond to the species listed above in the following manner:

ZnO based phosphors: claims 20-25
Y_2O_3 based phosphors: claims 26-32
$Y_3Al_5O_{12}$ based phosphors: claims 33-39
Barium aluminate based phosphors: claims 40-47
Metal silicate based phosphors claims 48-55

The following claims are generic Claims 1-19 and 56-107

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: The claimed species have all different compositions